THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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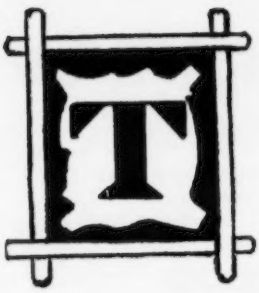

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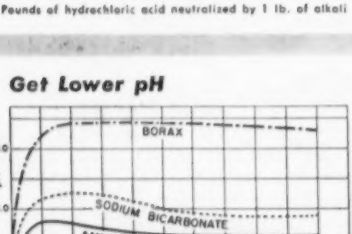

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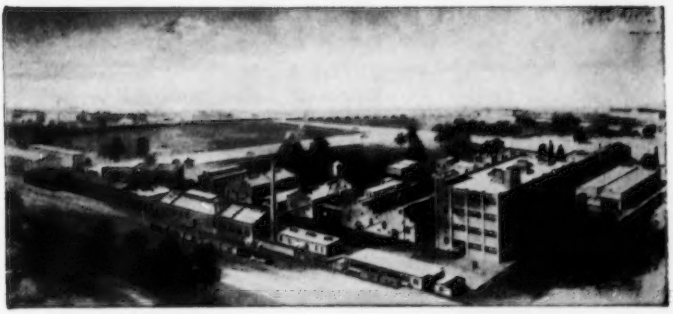

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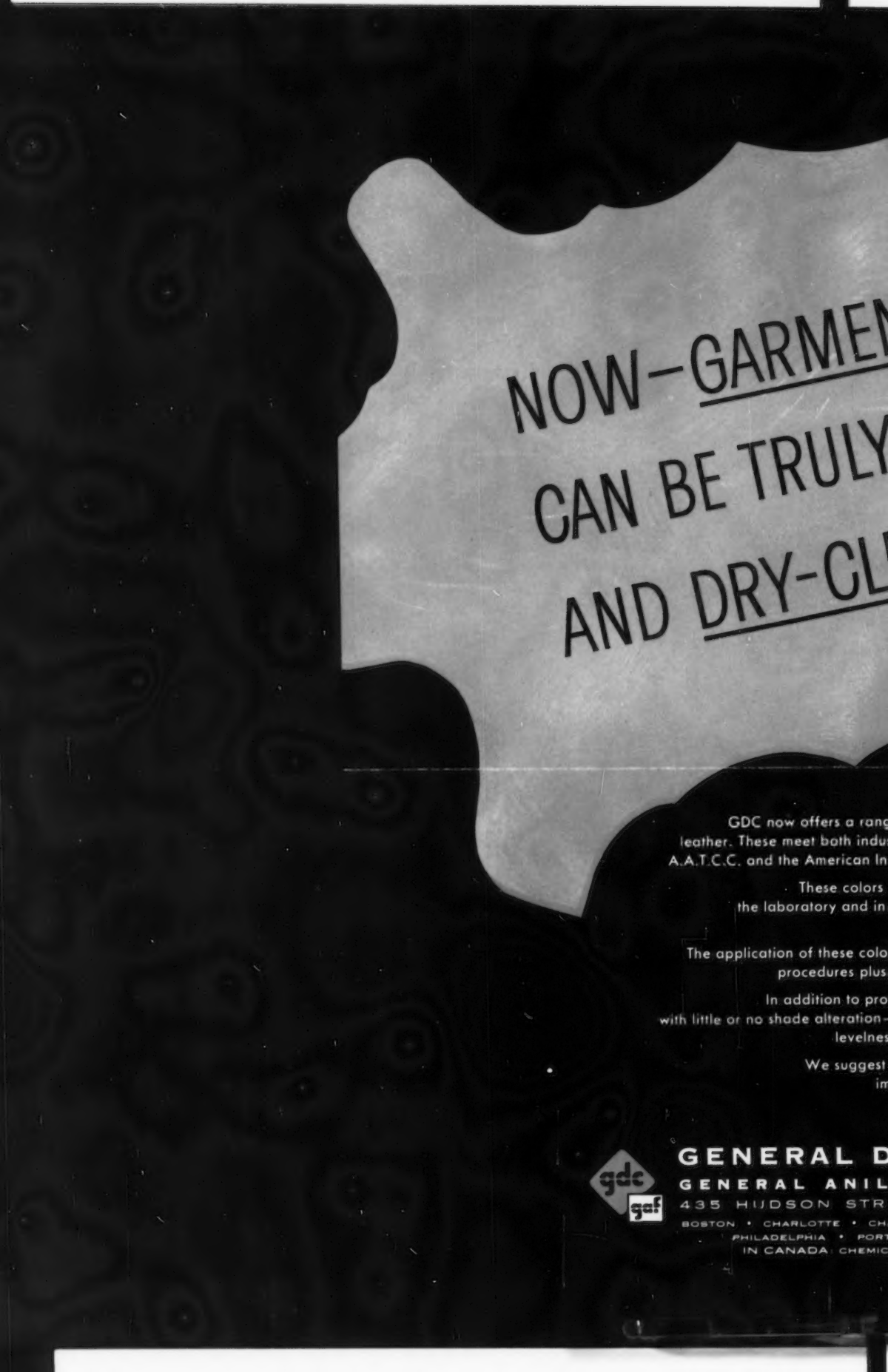
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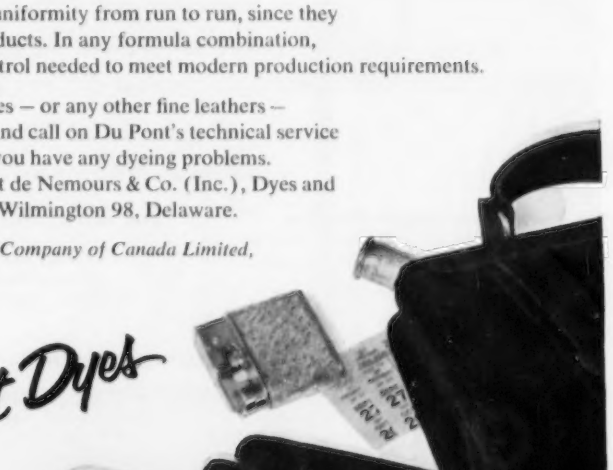

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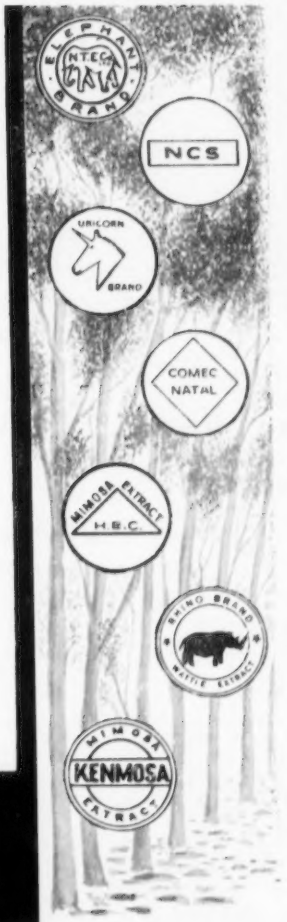

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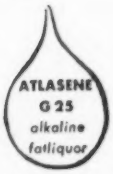

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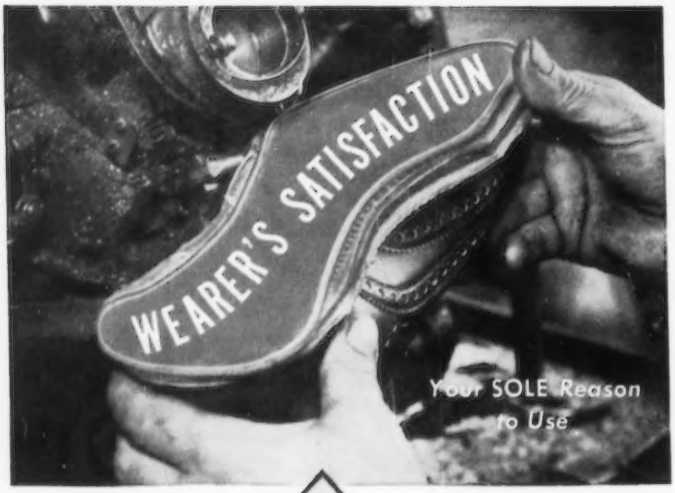

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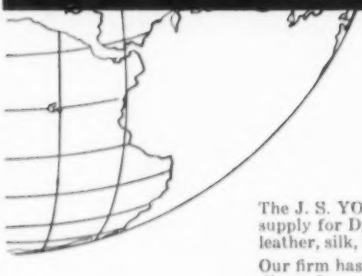

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for RUBBER TUBING

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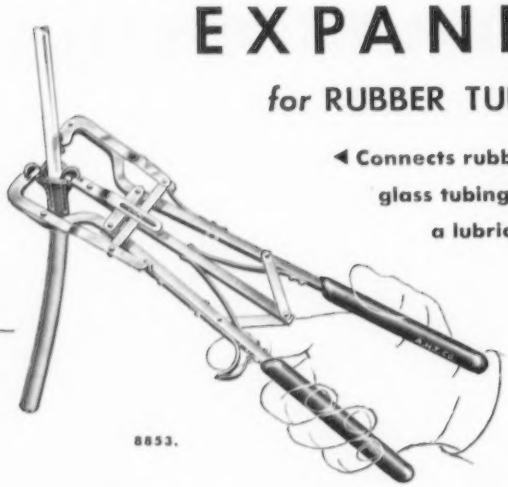

8853.

◀ Showing 12 mm o.d. glass tubing being inserted in ⅜-inch bore rubber tubing.

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To operate, tines are inserted into end of rubber tubing which can be spread open by squeezing the handles. The glass tubing is guided between and slightly beyond ends of the tines which are then unlocked by pulling a trigger. Tines are retracted without dislodging the glass tubing simply by repeating pressure on handles.

For use with rubber tubing from approximately ¼-inch to ⅜-inch bore. Not intended for use with pressure or vacuum tubing with thick, rigid wall, or with plastic tubings such as Tygon or polyethylene, which are less elastic than rubber.

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Some Aspects of Properties of Leather, from the Shoe Manufacturing Point of View*

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While the scope of my lecture is to discuss the properties of leather from the point of view of the shoe manufacturer, I should like to first express a few thoughts, which I find important for the present time, and thereafter go into the question of properties.

Leather is still one of the most important raw materials for the shoe industry and most of all leather which is produced goes into shoes. Shoe industry is therefore highly interested in everything, which is going on in the leather field, in the development of prices and particularly in the improvement of the quality in general.

As a matter of fact, footwear has become more and more an article of fashion and shoe industry has no more only the task to protect the feet against influences of climate and of ground, but has to satisfy the many desires of "Queen fashion", which often are very hard to meet. New forms, colors, combinations of materials have steadily to be brought out and products are to be produced, which suit the modern way of life. Still more daring constructions are required without neglect of the necessary mechanical stability of the shoe. As a consequence, the shoe manufacturer is compelled to select his raw materials more critically and to expect from them special properties. He first will call on his main supplier, the tannery. Where the latter is not in a position to meet special requirements as regards quality or price, he will have to look for other raw materials. To his regret he may be obliged to consider the price of raw materials more closely owing to the following fact:

Since the last war and in spite of the higher standard of living the clothing industry is getting a smaller share of the consumers' dollar, because there have since appeared so many things which make life easier and nicer and which have a predominance over the so called "soft goods". By these reasons we can watch in different sections a competition between leather and synthetic products, which sometimes turns out to get harmful to the leather, but which on the other hand has also brought some positive aspects.

Under the impression of events and of the advancement of synthetic products, many people feared that leather would soon be completely thrown out of the market. This is a wrong opinion. It cannot be overlooked that the synthetic products are necessary to fill a gap in the supply of leather. Cer-

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tainly all hides available in the free world are somehow transformed into leather and are not left to rot, but the increase in cattle population does not keep pace with the increase in men, and from this there results a lack of leather. In my opinion, leather will be made out of hides as long as their protein is not to be used for other purposes, be it for nutrition or otherwise. A pressure from the price-side is to be expected, and the leather industry may do well in preparing for a stronger competition.

Let us keep in mind:

Behind the synthetic products are enormous potentialities in capital and science, to which the tanning industry has by no means an equivalent.

As far as synthetics may have advanced towards the properties of leather, the unique structure of hide and leather has not been imitated. Here leather is still ahead, but for how long?

Alarmed by the intrusion of the synthetics into the domain of leather, leather people have gathered to meet the threat. Much effort has been made to improve the chances of leather, much money has been spent.

First, everywhere propaganda for leather has been started showing to the public what a useful, unique and beautiful raw material leather is and in what varieties it is manufactured.

There is no doubt that propaganda was a certain success, which, however, will not be lasting. Propaganda is one way and an expensive one. But there are others:

We have to get more knowledge of the finished leather.

We have to try to improve it where it shows deficiencies vis-a-vis the synthetic products.

We have got to use it where it is able to give special service thanks to its properties.

During the last years one could observe that the shoe manufacturers are getting more and more research-minded. Leading concerns have established their own laboratories or are about to do it. Shoe manufacturers started to discuss questions of materials within their associations, to consult Research Institutes and to subsidize them. They have started to meet with tanners, in order to set up standards.

Such endeavors are known in Europe and America.

What can we leather chemists do for the benefit of leather?

If we want to approach the problems of leather from all aspects, we must consider that we are in the first place not tanners, but scientists, whose relations to leather are different. However, just this fact that we are interested in leather from different points of view should enable us to discuss the problems in an efficient way.

The contribution, which we are to make to leather, is much more difficult and more painstaking than to make propaganda, and the number of chemists, who are able to work efficiently on this task, is limited,. We therefore have to concentrate our forces. We also need assistance from the circles interested in leather.

We know of leather chemists for over 50 years, their number having considerably increased during the last 3 decades. Considering the extent of literature about chemistry and technology of tanning, we must agree that much work has been done during that time.

Considerable improvement of our knowledge of the structure of animal hide, of collagen, its reactions as well as the principles of tanning processes has been reached. The most modern methods of analytical chemistry, of microscopy and electron-microscopy have been applied.

Most of this work is to be ranged in the field of fundamental research.

There were also published many promising reports about investigations in the tanning field. Unfortunately, most of them, however, give as a result only a few not very representative physical data about the samples of leather, obtained by these experiments. Others, reporting about physical properties of leather, failed in giving comprehensive descriptions of the kind of leather, which had been submitted to the tests. This did not give those papers the scientific weight, they otherwise would have merited.

Neither the tanning industry nor the leather consuming industry have been able to benefit in a corresponding measure by the scientific work and they are not to be blamed for this. Why?

In my estimation, the reason is that leather science is partly lacking a sufficiently sound practical foundation, that it is not rooted enough in the ground of leather manufacturing. What is needed is a bridge from science to practical tanning. The man in the tannery must get better tools enabling him to make sure whether or not and in what degree a change in his production will result in an improvement of his leather. Such tools, and I think of the most valuable, are physical methods for testing leather.

We have at our disposal a considerable number of analytical methods for the determination of the components of leather, but all these methods cannot consider the most important characteristics, namely the structure of hide and leather and the behavior of the fibers. Structure and condition of the fibres play a predominant role in the quality of leather.

You might reply: We already have many physical methods.

I am sorry to state that many of the existing methods have no regard to the specific structure of leather or the kind of service which is expected from it. Therefore, the results obtained by such methods are of little practical value. Those methods were often adapted from testing other materials than

leather, especially fabrics. We therefore must develop physical methods, which are suited to leather and its use, and I think that there must also be many dynamic methods. To find such physical methods is more difficult than is the case with chemical ones. It therefore would not be wise to try the same at different places and in different countries. A coordination of the work is very desirable, and here I see a chance for the Union of Leather Chemists Societies. We already have some international commissions sponsored by the Union. One is the Commission for Leather Analysis, which has been very active up to now and which would be able to take over the task of coordination. Of course, the work would have to be done by the national commissions and the results exchanged through the International Commission.

If it is the will of our Union to help leather more effectively, then in my opinion we should expand the work in the commissions. We should also reserve more time for them at our congresses and give them better consideration. At the same time we have to realize something else:

I mean the standardization of the methods for testing leather, the chemical as well as the physical ones.

There is already a certain difficulty in that we are speaking different languages, and the difficulties are increased by the fact that we apply partly very different methods and consequently get different results for the same property of the same leather. We therefore have got to standarize our methods as far as possible. The conditions for this are:

Willingness for cooperation,
Renunciation of personal or national reasons of prestige,
Scientific objectivity in the judgement of propositions.

Here again the Union will be only the platform for such endeavors. The Commissions of the Union have already successfully tried to work in this direction. Our appeal goes to every member to help us in these efforts.

The struggle of leather for its existence against synthetics requires from the tannery a quicker ability to meet the needs of the market. If we are considering this question from the standpoint of science, we might find for many of such problems a solution or explication in the literature. The tanner, however, is considering any changes in the processes with some hesitation, knowing by experience how detrimental such changes have occasionally turned out. This, especially, if it was disregarded that every step of the process must be in accordance with the preceding and following ones. Here again a control with suitable chemical and physical methods will be helpful.

Following these critical remarks I take pleasure in stating that the leather industry has shown much remarkable success during the last years.

Tannery has noted the tendency of the market for more flexible and lighter shoes and has succeeded in offering to the shoe industry leathers, which are

able to satisfy the demand in an appreciable measure. This concerns sole leather as well as upper leather.

Sole leather has become more flexible, lighter and more uniform in appearance. This uniformity has allowed an increase in the application of a natural looking stain on shoe bottoms, showing the beauty of leather.

Among *upper leather:* have appeared the soft, but good-standing materials for light unlined shoes, which are clothing the feet like gloves. These soft leathers are made out of different kinds of hides and skins and in different grains.

It is worthwhile to mention the progress in the manufacturing of fine-grained side leather, first brought out in U.S.A., following also in Europe, a progress brought by the Retan Leather and pasting method of drying.

This fine leather is a most welcome replacement for Boxcalf, which could not be supplied in sufficient quantities to meet the demand.

I further mention the Aniline Leather, which is preferred more and more. These are leathers dyed with aniline dye-stuffs and not covered with pigment finishes or only with translucent pigments. Since the introduction of pigment finishes for upper leather during World-War I, we have by this time become familiar with leathers, where the unique raw material could not be seen anymore, being buried under heavy coats of paints, plastic, etc.

Aniline Leather is the answer to that. It says something plastic cannot say: It is natural, it shows the beauty of the individual animal hide, it is a very strong promoter for leather.

There can further be noted a remarkable progress in waterproofing upper leather either by the Silicone treatment or by other processes.

The Properties of Leather

It is not in the scope of my lecture to deal with methods of analyses and physical testing of leather, these will be covered by other lectures. I, however, am intending to discuss the importance of some properties of leather from the angle of the shoe-industry.

There is a variety of different leathers being used for shoes. According to the application of these leathers for different purposes, various properties of the materials are to be considered. The main uses are for:

a. Soles and midsoles
b. Insoles
c. Counters
d. Uppers
e. Linings
f. Bindings, Hellcovers
g. Socklinings

The properties of leather are very complex and therefore difficult to describe. They are as a rule the sum of different single properties, chemical and physical aspects being interconnected. A separation of chemical and physical properties seems to be useless. There is no doubt, however, that the most important properties of leather are physical.

As already mentioned, I propose to deal only with those properties, which are, from the angle of the shoe industry, the most important ones. To start with, I do not differentiate between sole and upper leather, but intend to show the properties more or less common to both types.

Bearing in mind the application of leather for shoes, the properties might be assembled in 3 groups, namely:

A: Properties, which are important to manufacturing and durability of shoes in wear.

B: Properties responsible for the amount of comfort of the feet of the wearer.

C: Properties responsible for a good presentation of the shoe during wear.

Let us start with Group A:

Mechanical Properties (Shoe Manufacturing
Solidity in Wear)

- Tensile strength
- Tear—stitchtear - resistance
- Stretchability (distension)
- Plasticity
- Grain strength and stretch
- Resistance against continuous flexing (flexlife)
- Abrasion resistance
- Resistance against bending
- Suitability for cementing-process

Tensile strength is not very indicative. It might be useful for the testing of sole leather, especially for measuring any damage.

By reason of the big variation over the area of the skin, the determination of tensile strength is not useful for upper leather, it does not tell much.

Tear and stitchtear are of more value and subject to less variation over the area of the skin.

As to upper leather and linings it is important to know the relation between load and distension, together with the amount of permanent distension. The latter plays a role in the durability of uppers as well as on molding leather soles. It gives a measure of the plastic deformation at a certain tension and could be called "plasticity" of leather, a property very important in the scope of shoe manufacturing.

The determination of distension with dumb-bell-shaped test pieces or strips may be useful with heavy leather, but gives unrealistically high values with upper leather, caused by high contraction of the strips in the cross section. Distension of upper leathers should be determined in an apparatus similar to the Mullen-Tester or Lastometer.

We are using an instrument where air or oil pressure is applied to a clamped disk of leather, whereby pressure and distension are recorded on a graph. There is no necessity of bursting the leather, because the first part of the curve is characteristic and important. By releasing pressure and repetition of the test, a measure for plasticity is obtained. Tests are also executed at different degrees of humidity.

Crackings of grain, of course, are carefully watched and registered. This test is giving a very useful indication about the behavior of a leather on lasting.

Tear and stitchtear resistance and bursting strength should only be expressed by the tearing load, not considering thickness of the specimen. There is no relation between heavier and lighter skins in a pack and the comparability of results is therefore unduly diminished if leather thickness goes into the calculation.

To know grain strength and stretch is of first importance for many applications of upper leather. There are two methods to be considered:

1. The one just described with the Bursting Tester
2. An impact test, where a hammer falls on the edge of a folded piece of leather.

Both tests should be applied accordingly.

The flexlife of upper leather, the resistance against continuous flexing, has ever been considered as significant. However, adequate methods for such tests were not available until recently.

Dr. Kanagy has published a method, developed at the National Bureau of Standards, Washington. The Bally Flexometer has been built on a different principle.

Good abrasion-resistance is important for sole leather. Different methods are used and here again the most suitable one has to be found out and to be standardized.

It has already been mentioned that today most soles are attached to the uppers by cementing instead of stitching. This pertains to upper- and sole-leathers, which can readily be roughed, leaving a willow surface where the cement can grip. The condition is an open texture of the leather fibres enabling the tools of the roughing machine to penetrate and separate the

bundles. It is significant to mention that there are many sole leathers on the market, which do not meet this requirement.

Group B:

Properties responsible for comfort of feet

- Flexibility
- Permeability for water-vapor
- Permeability for air
- Waterproofness
- Thermal conductivity (insulation)
- Condition of surface (linings, insoles)
- Freedom from substances causing irritation of skin.

Flexibility of sole leather and upper leather is essential for modern footwear. A good method for its determination has still to be found.

Considering permeability for air and water-vapor, we must stress upon the preference of the latter. This applies to sole leather as well as to upper leather. Water-vapor permeability is much more contributing to comfort and health than air-permeability.

A property often discussed is waterproofness. A really waterproof leather was unknown until recently. Silicone treatment has brought considerable improvement and changed the situation. However, it is a new process, and as the time for experience in the field has been relatively short, a certain reserve is advisable.

It is well known that Silicone does not work as well on every tannage, even not on every chrome tannage. Furthermore, an application on a broader scale is still a question of price.

There should further be mentioned the Quilon treatment (Dupont), which has proved promising for Suede leather and another process, called "Bavon" (Battelle Devel. Co.).

These 3 new methods have, besides the better results in water-proofing, two big advantages over the stuffing:

1. They secure to a certain degree the water-vapor transmission, which is considerably reduced with stuffed leathers.
2. The treated leather still contains a good amount of air, hence better thermal insulation and lower specific weight.

All endeavors in waterproofing sole leather have not been very successful to the present time. Impregnation of sole leather with rubber or plastics is not likely to be the answer. Such a leather would probably have little value over plastics.

As a consequence of the successes in waterproofing upper leather, the testing

for water resistance has again aroused an increasing interest. Any method to determine water-resistance of leather should be a dynamic one.

Thermal insultation has to be low for summer- and high for winter-footwear. Good insulation requires air entrapped between the fibres. Better heat transfer is secured by high water-vapor permeability.

The condition of the surface of the inner parts of shoes, like linings, insoles and socklinings, is an important, but so often ignored factor for comfort. These parts, being in close contact with the foot, can have an influence to the feeling of the foot, which overbalances the effect of water-vapor permeability. A surface too smooth with a low frictional coefficient might give the foot not enough hold and cause irritations by the steady friction between shoe and foot. Many complaints of "burning feet" can be explained by such a condition.

Of course, leather has to be free from substances, which could cause irritations of the skin of the foot.

Group C:

Properties responsible for appearance of shoes after certain wear

Fastness to light
Fastness to dry and wet rubbing and bleeding
Fastness to action of water
Resistance against action of perspiration
Resistance against action of microorganisms
Suitability for easy "make-up"
Freedom from substances causing spues on leather
(fats, salts, glucose)

Requirement No. 1 is to avoid any discoloration whatsoever: Fading of color at sun light, crocking or bleeding of finishes, staining by the action of water or perspiration.

Light fastness is not required as high as for certain textile products. A medium fastness will be sufficient, say 4 to 5 in the standard wool list. But you can find shades in the market, so sensitive to light that they were better used for printing photos than for shoes.

Pigment finishes on water base are frequently not sufficiently fixed and come off when rubbed wet.

Aniline leather has brought many difficulties by reason that the dyestuffs are sometimes not entirely fixed on the fibres and tend to stain the leather when it is slightly wetted by rain or perspiration.

The resistance of leather against perspiration has recently received more consideration. This applies to insoles, linings and upper leathers. The problem has been brought up by two reasons:

1. The light Nylon stockings do not absorb enough sweat, and it even has become fashionable to wear summer shoes without stockings.
2. It is the trend of fashion to wear unlined shoes, where the upper leather is not protected and more exposed to perspiration.

One measure to reduce the pernicious action of foot perspiration is therefore to impart to the leather a certain water repellency, so that sweat is not transferred through the leather in liquid form.

Another measure is to use better sweat resistant leathers, which are thoroughly chrome tanned or chrome retanned linings and upper leather, chrome retanned insoles or such vegetable tanned insoles, which have received a final treatment with Formaldehyde or Alum.

Another claim for leather is its freedom from substances, which could cause spues or stains at the surface. Here may be mentioned: Solid fatty acids, heavily oxidizing oils, water soluble salts, sulphur, sugar.

In order to show a nice appearance, shoes need some care, first before leaving the factory and consistently during wear. This "make-up" will be more or less impressive, depending upon the character of the leather. In any case, it needs a highly skilled tanner to impart this property to his leather.

To reach a good lustre is a question of development of the grain as well as of good finishing.

In order to get a realistic picture of the value of a certain leather, we will have to measure as many as possible of the main properties and to compare them with settled standards. These standards can only be fixed if we are able to measure the stress and strains leather has to suffer during shoe manufacturing and wear. This determination is, although sometimes rather difficult, in most cases feasible. And only by basing on this fundamental knowledge will it be possible to set up standards. Still more difficulties are met on trying to imitate, in the laboratory, the strains to which leather is subject on wearing of shoes. New equipment has to be designed for this purpose and its performance must be controlled by wear tests.

Concerning the value of the chemical analysis of sole leather, opinions differ. Whatever the attitude may be, it is important to know the amount of water soluble matters, organic and inorganic, and the acidity.

With flexible sole leather the amount of water soluble matters has to be low, in order to avoid damages of light upper leathers, if by wet weather water is sucked into the upper from the wetted soles. This water might transport considerable amounts of free tannin and salts into the upper leather, causing discoloration, hardening and cracking of the latter.

The same applies to insoles, which can cause the same trouble, if they contain much water solubles, especially salts . Besides that, insoles are supposed to absorb quantities of perspiration, hence they must be of open structure and not charged.

Considering the use of tannin fixing agents, the content of hide substance per unit of volume of the leather will get more consideration. Nitrogen containing agents have to be stripped before determination of hide substance.

The main problem with the modern flexible sole leather is its increased water permeability. It might not yet show up today in its full meaning because so many rubber- and synthetic soles are applied to Street- and Sport-shoes. However, if as we all want, leather soles regain importance in the future, this problem has to be solved. In my estimation, sole leather will only have a chance, if it is flexible *and* water resistant.

With upper leather, the complete chemical analysis is still playing a minor role. Some single tests, however, are necessary and frequently applied. There has to be determined the kind of tannage and finish, the amount of water soluble matters, the acidity and the content of fat. These determinations are still more frequently made from 3 and more layers of the leather (stratographic analysis) and I would like to stress the importance of this procedure, the knowledge of the distribution of the components over the cross section of the leather being very indicative.

Although the tanner might be interested in knowing the amount of chrome in a leather, this is less important for the evaluation of its properties by the shoe factory.

The degree or intensity of tannage is indicated by the shrinkage temperature and the behavior at the boiling test. Experience has shown that leathers with a high shrinkage temperature also resist better the action of foot perspiration.

In the trade the quality of any leather, preferably upper leather, is still judged by craftsmanship, that means, the experts know from the feeling and looking at a leather what it is worth. They have acquired this ability by years of experience. Can their opinion always be right?

As scientists we want to measure and get reproducible figures. The principal difficulty, however, with this testing is that our instruments, even if they give reproducible figures of sufficient accuracy, may not measure just the property the craftsman wants.

Will he understand the figures, the scientist presents him, and do the determined criteria really indicate the requirements of the industry?

What do expressions mean like "body", "touch", "plasticity", "temper" of a leather in physical terms? How to measure them?

These are questions to be seriously considered by everyone who wants to test leather.

The Sewage Problem in the Leather Industry*

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West Germany

The problems of industrial sewage have been discussed theoretically and in the literature for the past thirty years. It has been recognized that a wholly new approach is needed to the hitherto exclusively considered question of municipal fecal sewage, if one is to work with industrial sewage. The predominantly biological-mechanical approach which has prevailed with such great results in the case of municipal sewage, has to be replaced by thinking along chemical lines. From the concept of "clarification", meaning mechanical clarification, and the "clarification works" associated therewith, we must move on to "purification", by which chemical purification usually is meant.

Unfortunately this line of thought is not in agreement with current practice. On the contrary, even today, mechanical clarification plants in industrial establishments are not merely recommended but actually required by the authorities. The fault lies in the one-sided training of the technical water and sewage authorities, which is concerned solely with municipal fecal sewage. The inevitable result is that these officials cannot comprehend that a clarification works, designed and built according to all the rules of the art, leaves untouched the soluble chemical poisons that may have been introduced into the sewage. Then, lacking chemical knowledge, and above all lacking any insight into the manifold different processes of industry, they demand yet bigger and more expensive—but naturally just as ineffective—clarification plants. The representatives of officialdom, being aloof from production, could not in the past readily solve the problems of industrial sewage. These have been, and are, being solved through the cooperation of individual factories or industrial groups, who must themselves undertake the purification of their sewage as an internal problem.

Recognizing that sewage purification is a technical problem of the industry itself, the Association of the German Leather Industry resolved to take in hand and put to use the procedures that had previously been worked out and proved in practice in individual cases. Then, in cooperation with the authorities, the over-strict and in part unsuitable regulations could be put right, and requirements and projects set up that would be practically effective for

*An address delivered at the Fourth Biennial Conference of the International Union of Leather Chemists' Societies, Stockholm, Sweden, August 1 – 4, 1955. Translated and published by permission of the author. While this address, and the statements made therein, apply particularly to the conditions that exist in the heavily industrialized regions of Western Germany, it is felt that the readers of this journal will be interested in this example of current European thought with regard to a problem that is becoming increasingly serious in the United States.

Translated by H. B. Merrill.

tanneries, and above all economically bearable. It should be stated that the current officials are glad to be advised and instructed. This cooperation between the industry and the public servants has worked to the advantage of both sides. The supervisory officials can, in case after case, confirm the purification of tannery sewage, and the manufacturers are astonished to find how practically and cheaply they can arrive at this result.

Because the Association of the German Leather Industry in West Germany is dealing with the sewage problem as a self-administered task, a Department of Water and Sewage has been set up within the West German Leather School at Reutlingen (J. Wagner, Director), through which the appropriate investigations will be undertaken for tanneries. It is noteworthy that already plants of other similarly situated industries have made use of this service to good advantage; the glue industry and the textile industry are examples.

It is not possible within this scope of this article to deal with all questions of a chemico-technical nature. We can only indicate by key words the individual question-complexes that are tied up with tannery sewage. First of all, however, it must be established that there is no such entity as "tannery sewage". If one compares the working procedures of an upper leather tannery, with its strongly alkaline unhairing liquors usually sharpened with sodium sulfide, and those employed in finishing imported, vegetable-tanned skins that need only to be colored and finished, one will get an insight into how widely the qualities of the sewage can vary. These different kinds of establishments, differing in raw materials, processes, and end products, are not to be considered together with respect to sewage. Likewise regional differences in water supply, which are well known to bring about such clear differences in regional tanning methods, have a decided influence on the qualities of the sewage. The content of aggressive, unbound carbon dioxide, and the degree of hardness, play important toles. For example, when hard wash water, which is used in large quantities in the beamhouse, is mixed with the lime liquors, the so-called "involuntary softening" takes place, leading to abundant precipitation of calcium carbonate. In other places the free carbon dioxide in the wash water may affect or even prevent the subsequent desired binding of hydrogen sulfide (from the lime liquors). It is further to be recognized that the purity standards established by the authorities depend very largely on whether a factory discharges its sewage into a brook or river, or into a municipal clarification plant. Also, the capacity of the stream for self-purification plays a great part. By including this factor in the overall estimate of the situation, the tanner can help to economize on his own costs.

To summarize: So-called "tannery sewages" differ from each other, first with internal tannery conditions (raw stock, processes, end products); second in consequence of locally different water supplies; and in the third place the particular disposal stream or municpal disposal plant requires especial at-

tention. For these sorts of heterogenous relationships, no "Procedure for The Purification of Tannery Sewage" can be worked out. We, in West Germany, have no such patent solution. We have, more modestly, confined ourselves to working out the individual facts in one case or another. In every plant fundamental research is needed before anything can be said about sewage treatment. Perhaps I may be permitted to use a simile. We have worked out and collected individual facts, which we may compare to mosaic tiles. How these are to be assembled to make a complete picture (that is, give a workable sewage purification process in any individual case), that is always a new problem for every tannery concerned.

Now let us mention a few of these mosaic tiles.

In most plants, the relatively harmless or scarcely polluted rinsing water of the beamhouse is mixed with the heavily polluted types of sewage. This by no means removes, or renders innocuous, the chemical and biological poisons. Sodium or arsenic sulfide from painting or liming, the high alkalinity of the limes, the spent vegetable tan liquors (sometimes poisonous, more often merely a nuisance because of the formation of blue-black compounds with iron in the disposal stream), the always poisonous chromium, the irksome dyestuffs, these are not removed by dilution. On the contrary, the manufacturer makes the purification more difficult for himself because he must struggle with a diluted, but enormously increased sewage flood, purify it, and last but not least pay for the job. It may be remarked in passing that, in general, much water could be saved in the beamhouse and the wash drums without impairing the quality of the product or slowing up the work. It can be taken as the normal condition that 80 per cent of the total waste water needs no purification. In several cases we have been able to economize on the use of water, through attention to little technical details, and thereby accomplished an improvement. Furthermore, we secured permission from the authorities to discharge the unpolluted wash water without treatment. The resulting relief to the tanneries was appreciable.

Sharpened lime liquors are extremely dangerous and poisonous both from their high alkalinity and their content of colloidal proteins. That the arsenic- or sodium sulfide must be rendered inactive is always to be understood. The methods we have set up (precipitation as FeS or oxidation of the sulfide to "oxysulfide" or free sulfur) are practical and cheap. The treatment with iron salts also does away with the caustic alkalinity resulting from the hydrolysis of sodium sulfide. It is recommended that the lime liquor sludge be trapped in little lime-catching pits, whereby the remaining alkalinity of sewage flowing over these pits will be reduced. The removal of colloidal proteins, which flocculate rapidly at pH about 8.5, reduces the $KMnO_4$ value by as much as 85 per cent. Because the analytical characteristics of fecal sewage are not directly comparable with those of industrial sewage, on account of the different make-up of the latter, we should be reminded that

such earlier used conceptions as "resident equivalent" are not applicable. Likewise the "BSB_5" (biological oxygen demand) is not a valid standard. If chemical reducing agents that in themselves consume large amounts of oxygen are present when the B. O. D. measurement is made, one arrives at altogether false and much too high values. If then the sanitary authorities figure the cost of treating the sewage on the basis of B. O. D. values obtained on domestic sewage, the error is all too clear, and the leather industry, unfortunately situated in this respect, must carry the load. If we wish to establish a standard for the purification of our sewage, the lowering of the $KMnO_4$ value affords an index. If this value has been lowered by 50 per cent, then the factory has on its own part made a considerable contribution. The before-mentioned detoxification (inactivation of sulfides) contributes to this (lowering of the $KMnO_4$ value).

Vegetable liquors, pickles, and chrome tanning liquors are produced in smaller amounts. By combining them with the spent lime liquors, their purification is accomplished without difficulty.

Dye liquors, in general, are decolorized by fixation of the dye by the precipitated proteins from the lime liquor treatment.

The inorganic pigment dispersions that are so much used in pigment finishes, with ever increasing additions of synthetic colloids (resins), get into the sewage only in minor amounts, from cleaning out containers, spray guns, etc. However, they should not be ignored, any more than the colloidal proteins of the lime liquors.

A word now about anthrax. According to annual statistics, anthrax occurs least of all in tanneries. Meat handlers, slaughter house workers, loaders of exotic skins in foreign ports, and hide handlers are far more liable to this disease than tannery workers. The fact that, in spite of this, tanneries bear the odium of anthrax as an occupational disease is due to statements in text books that are carried forward uncritically from one edition to the next. At any rate, in the wet work, and in the always alkaline beamhouse sewage, there cannot be any question of danger from anthrax. Unfortunately, frequent and thoughtless statements are made concerning the danger of anthrax from sewage irrigation. This is contrary to the facts, and is hereby designated as false.

We have, in a series of leather factories and tanneries in West Germany, been able to accomplish the sewage purification in accordance with the particular circumstances to the satisfaction of the authorities and at small cost to the companies. The principles that we have named were applied entirely differently in the several developments, so that we can by no means speak of a fixed "procedure". In one notable case it was necessary to clarify completely the entire sewage on the manufacturer's premises. No wash water could be separated, and the small brook adjoining the plant had too low a

self-purification capacity to be taken into account. There we installed a plant that has now, for 7 consecutive months, delivered a fully pure and clear effluent to that brook, with a daily flow of 5000 cubic meters. I think this is the first case of large scale complete purification of tannery sewage by itself, with all the usual impurities present (soaks, limes, vegetables and chrome tan liquors, color room liquors, and spray finishing wastes). This shows that it is practicable to purify this especially dangerous and troublesome sewage without mixing it with other types of sewage. It is planned to extend this information to other similar branches of industry in the federal republic (glue factories, textile factories, dairies), and thus install economically tolerable and technically workable sewage purification in such establishments. The Department of Water and Sewage of the West German Leather School at Reutlingen has already taken steps in this direction.

Prevention of Microbiological Deterioration of Leather†*

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ABSTRACT

The prevention of microbiological deterioration of leather starts with the freshly flayed hide. Any destruction of collagen by bacteria prior to tanning cannot be compensated for by the tanner's skill and experience, and will result in inferior leather. The methods used for protection of the hide prior to and during tanning operations are briefly discussed. Tanning makes collagen resistant to microorganisms, but leather adjuncts, such as oils and greases, are excellent nutrients for molds, especially *Aspergillus niger*. Due to the removal of leather adjuncts by such molds, the leather becomes stiff and brittle, and its usefulness is impaired. Fungicides are now being used to prevent this deterioration. Methods used for the evaluation of fungicides for this purpose, and the types of compounds found to be most effective, are discussed.

1. INTRODUCTION

Finished leather, and animal skins from which it is made, are very susceptible to microbiological attack. The leather-making process is, therefore, one in which microorganisms are important factors. Generally, but not always, microbiological activity in leathermaking is harmful and has to be prevented or at least controlled.

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The animal skin contains a great variety of microorganisms which are derived from air, water, soil, manure, and extraneous filth. While the animal is still alive, most of these organisms have little effect on the skin. But after removal of the skin from the dead animal, during which operation the flesh side also becomes contaminated, these organisms find themselves in a perfect medium for growth and almost immediately start multiplying at an enormous rate. Putrefaction would soon destroy the skin structure if nature were permitted to take its course. By tanning, the skin is, among other things, made resistant to putrefaction. However, if microbiological damage to the skin occurs prior to tanning, inferior leather will be produced, no matter how well the tanning is done. Prevention of microbiological deterioration of leather, therefore, may be considered to start with prevention of such damage to the skin shortly after it is removed from the dead animal.

The subject of this paper may conveniently be divided into two parts: (1) deterioration of the skin prior to and during tanning; and (2) deterioration of finished leather. The first part is something that has always been a problem in leathermaking. It is concerned mainly with proteolytic bacteria. The second part has become a problem of interest in recent years, though it has, of course, always existed. It is concerned mainly with fungi.

2. Deterioration of Skins Prior to and During Tanning

2.1 *The Leathermaking Process.*

The main steps in the processing of a freshly flayed skin or hide into finished leather are listed below in the order in which they occur in the process. The object of the various steps are briefly indicated.

A. *Curing*: Preservation of the skin until it gets to the tannery.

B. *Soaking*: This is the first tannery operation and consists of softening up and rehydrating the partially dehydrated cured skin. It also serves to remove blood, soluble proteins, dirt, and manure from the skin before further processing.

C. *Liming and unhairing*: Swelling and conditioning of the fibrous skin proteins, and removal of the hair.

D. *Bating*: Enzymatic removal of interfibrillary proteins, and deliming of the skin.

E. *Pickling*: Uniform conditioning of the skin for subsequent tanning. Also, preservation of the skin until tanning.

F. *Tanning*: Alteration of the skin protein, collagen, so that it becomes resistant to putrefaction and enzymatic attack, water insoluble, and more

stable to heat. All of these changes are presumably due to cross linking of the collagen peptide chains by the tanning agents.

G. *Oiling*: Incorporation of oils and greases into the leather.

H. *Finishing*: This includes a number of treatments designed to produce the specific properties and appearance of a given type of leather.

Most of these steps include chemical and physical factors interacting so as to make the whole process very complex. The results obtained in one step generally also influence those produced in successive steps. Action taken to control the microbiological balance must not adversely affect the process as a whole. In spite of much research and study on the conversion of skin into leather, the changes taking place are not well understood. The aim of the various pretanning steps is to preserve, purify, and condition the net-work of collagen fibers in the skin. In order to facilitate the tanning reaction, non-fibrous proteins, fats, and other skin components must be removed. Limited microbiological activity that attacks and helps remove the unwanted components is desirable. But such limited activity is difficult to control and is apt to damage the collagen also. For that reason total prevention of microbiological growth is nearly always aimed for in leathermaking, though probably never completely obtained.

Information on the art and science of leathermaking, including microbiology, is available in a number of books on the subject [1]. In this paper only parts that are thought pertinent to the topic of this discussion will be reviewed.

2.2 *Curing and Soaking*

Curing and soaking are two operations particularly important from the point of view of microbiological deterioration of the leathermaking material of the skin. The curing should be such that the changes caused by it can be reversed and the original condition of the skin brought about by the subsequent soaking operation.

(a) *Curing*

Two general types of curing are used: (1) air curing and (2) salt curing. The preservation action of both is based on dehydration of the skin, thus depriving the bacteria of water necessary for their growth. The water content of a fresh skin is about 60 per cent. By air curing, which consists simply of drying the skin in air, the water content is reduced to about 15 per cent. If done properly, it preserves the skin almost indefinitely if the skin is stored under dry, cool conditions. The drying should be slow enough so that interior water will have a chance to escape before the flesh side becomes too dry and impenetrable. Water enclosed within the skin may result in damage due to

putrefaction by anaerobic bacteria. Air cure is used mainly in countries with a dry, hot climate, or in primitive countries where salt may be expensive or unavailable. One disadvantage of air curing is that the nonfibrous and fibrous proteins during the drying become glued together into a hard mass which then requires a long subsequent soaking operation at the tannery.

Salt curing may be accomplished either by dry salting, in which the flesh side is covered by a layer of dry crushed sodium chloride, or by treatment of the skin in brine. The latter is preferable because it also serves to remove blood, filth, and bacteria from the skin, thus lessening the oppotunity for putrefaction to develop. In either application, brine penetrates through the skin from the flesh side, replacing water by osmotic action. The water necessary for bacterial growth is thereby removed. About 12.5 per cent of salt should be deposited in the skin for adequate protection, calculated on skin weight when moisture is about 40 per cent. These percentages are for freshly salted heavy skins or hides. The moisture content may be considerably reduced by partial drying.

During salt curing, a considerable portion of the nonfibrous proteins is dissolved and removed by the brine. The collagen fibers are not glued together. Salt-cured skins, therefore, require a much shorter soaking period than air-cured skins. Salt curing is commonly used by meat packers in this country, and numerous studies on the various details of this method have been supported by them, with the purpose of finding the most practical and effective way of application for the various types of skins [4, 5, 22].

In either type of cure, many of the bacteria that were originally on the skin are not killed. Isolation and identification of all microorganisms that may be found on hides and skins would probably be an endless task. It would vary greatly with the environment of the animal.

The organisms recently reported as the normal flora of fresh salted calfskins [2], together with the salt tolerances found for the respective groups, are as follows:

Normal Flora of Fresh Salted Skins

Taxonomic group	Strains	Salt tolerance
Achromobacter	18	Sensitive
Micrococcus	24	Very tolerant
Sarcinae	4	Very tolerant
Staphylococcus	28	Very tolerant
Bacillacee	8	Fairly tolerant
Rhodococcus	2	———
Unclassified	7	———

All bacilli, seven strains of *Staphylococcus*, and 10 strains of *Achromobacter* were found to be able to liquify gelatin. Only the bacilli digested collagen

directly, and according to this report [2], are responsible for the early stages of skin putrefaction. No intestinal organisms or any organisms of the *Proteus* groups, all of which are prevalent on fresh unsalted hides, were found on these skins. Tests showed that these organisms are very salt sensitive and that most of them are probably killed by the salt curing.

(b) *Soaking*

As was previously mentioned, soaking, which is the first treatment of the skin after it reaches the tannery, is for the purpose of restoring the dried or salted skin to its original condition. Obviously, the method used in curing determines how this is to be accomplished.

Air-cured skins are very resistant to penetration by the soaking solution due to the great amount of coagulated proteins and blood that they contain. Such skins require a long soaking period. The longer the soaking period, the greater is the chance for bacterial growth with risk of damage to the leather-making material. Some slight putrefaction of the skin nearly always occurs during the early stages of drying, so a heavy infection with bacteria generally prevails. These organisms find an ideal environment in the nitrogenous breakdown products, coagulated proteins and blood dissolved in the soak solution. Three functions are required of a soak solution for dried skins. It should (1) inhibit bacterial growth, (2) disperse coagulated interfibrillary proteins, and (3) assist the rehydration of the collagen fibers. Plain water is unsatisfactory for this. Chlorine is often added as the antiseptic agent, generally in the form of sodium hypochlorite. Various weakly-alkaline salt mixtures are often added for accomplishing the desired results. Wetting agents are also sometimes used for the purpose of aiding penetration of the skin by the solution, thus shortening the soaking time required.

Salted skins are much easier to soak than dried ones since in the former case a large portion of the coagulable protein has already been removed and the collagen fibers are comparatively easily rehydrated. An additional function of soaking these skins is the removal of the salt deposited in them. Only a comparatively short soaking period is required, but some antiseptic agent, such as hypochlorite, is generally used.

2.3 Salt Stains and Red Heat

Stains and discolorations that are difficult or impossible to remove and that reduce the sales value of the leather are sometimes encountered on salt-cured skins. Salt stains and red heat are the trade designations for these defects. Both are now thought to be caused primarily by the growth of chromogenic, halophilic organisms.

Salt stains vary in color from brownish to green-blue. They are seldom found on brine-cured skins, but often on dry salted ones, especially on skins

that are very dirty. Addition of a few per cent of sodium carbonate to the salt has been found an effective preventive of salt stains, probably by producing a pH in the skin too high for the growth of these organisms.

Red heat is a pinkish, red, or purple coloration on the flesh side of the skins. The bacteria causing this defect are able to grow at a high pH, and are not inhibited by the addition of sodium carbonate. These bacteria, some of which have been identified as species of *Sarcinae* and *Micrococcus*[10], are apparently introduced as contaminants in marine salts.

Sodium silicofluoride has been recommended as an effective and practical preventive for red heat in salt curing[11, 12, 13, 14].

2.4 *Microbiological Activity in the Rest of the Leathermaking Process*

(a) *Liming*

In liming and unhairing, in which the skin is treated with a solution containing calcium hydroxide as the principal constituent, the pH is too high for any appreciable microbiological activity.

(b) *Bating*

Proteolytic enzymes, some of which are of bacteriological origin, are utilized in bating for the purpose of removing interfibrillary proteins. Such enzymes are now commercially available and are added to the bating solution, together with ammonium salts and organic acids. The purpose of the latter is to react and neutralize the lime remaining in the skin. The use of synthetic enzymes is of comparatively recent origin. Thirty to forty years ago, bating was accomplished by preparing an infusion of manure in which proteolytic enzymes were present. Fermentive bacteria, also present in the manure, produced organic acids in such natural bates. If bating proceeds too far, destruction of the leathermaking proteins will occur. But with the present type of bating this cannot be blamed on microorganisms as it could be when the natural bates were used.

(c) *Pickling*

The pickling solution generally used is a mixture of sodium chloride and sulfuric acid. About 12 per cent salt and 1.5 per cent sulfuric acid constitute a satisfactory pickle. This solution has a pH too low for bacterial growth. Acid alone would cause the collagen fibers to swell by taking up water. Salt counteracts the acid swelling and at a concentration above about 6 per cent actually causes dehydration of the skin, thereby also acting as a preservative against putrefaction.

Pickled skins may, therefore, be stored for a considerable time before tanning. During storage, those molds that are able to grow in acid media

may attack these skins and cause damaging stains and destruction of the skin by the proteolytic enzymes they produce. Addition of small amounts of organic acids or salts of organic acids to the pickle solution improves its preservative power against molds. This is explained as being due to the lower degree of ionization of organic acids, compared to inorganic, and greater ability of uncharged molecules, compared to ions, to penetrate the cell wall of the organism[1a].

(d) *Tanning*

Among the various types of tanning agents used, the one of greatest concern from the standpoint of microbiological deterioration is vegetable tannin. Bacteria, yeasts, and molds are all commonly found in vegetable tanning liquors. Yeasts and some bacteria may be beneficial in that they produce organic acids, such as lactic acid and acetic acid, through fermentation. These acids are desirable for attainment of the proper pH of the liquor. But tannin may also be destroyed by such fermentations, and in some stages of the process bacterial growth may even be destructive to the skin fibers. Therefore, it is safer to add the necessary organic acids and to prevent fermentation and other microbiological growth by the addition of preservatives. Molds, especially *A. niger*, are also commonly found in tan liquors, and if their growth is not prevented, the tanned leather will be impregnated with spores. Such leather will then be especially susceptible to mildew growth after it is removed from the liquor. Preservatives commonly used in tan liquors are cresols, naphthols, sodium silicofluoride, and *p*-nitrophenol.

3. Deterioration of Finished Leather

3.1 *General Considerations*

After the leather is finished and leaves the tannery, it may be damaged by mildew growth if stored under hot and humid conditions. *A. niger* is an organism commonly found in leather mildew. Penicillium and others have been isolated [19, 24]. Probably a great number of additional ones are involved.

Prior to World War II mildew growth on leather was considered of relatively little importance. Very little effort was made to prevent it before the employment of large military forces in tropical areas made it a factor of great economical importance.

Studies made in this country [3, 8, 9] and in England [7, 19] during World War II and afterwards showed that the main effect of mildew on leather is the removal of greases. This causes stiffness and loss in tensile strength. The useful life of leather items stored or used under conditions favorable to mildew growth is thereby shortened although collagen, the hide protein, apparently is not directly degraded [3].

p-Nitrophenol is now the preferred fungicide for the prevention of mildew on finished leather[10,15,23]. Since 1951 it has been required in footwear leathers procured by the Quartermaster Corps. A concentration of about 0.3 per cent (based on dry leather weight) is used. This amount is adequate for the protection of all types of leathers under severe storage conditions. Vegetable-tanned leather is the type most susceptible to mildew attack, and any fungicide concentration that mildewproofs this type of leather will also protect any other type, such as chrometanned, retanned (combination of chrome and vegetable tannage), syntan, etc. A chemical test method has been developed[16] for ascertaining that the concentration of *p*-nitrophenol in the leather conforms to specification requirements.

3.2 *Mildewproofing of Leather with p-Nitrophenol*

(a) *Tannery Treatment of Hides*

In tannery operations, *p*-nitrophenol is generally introduced into the leather together with greases in which it is soluble. Data have been published on the solubility of *p*-nitrophenol in various leather lubricants[18]. As is well known, the porosity of a hide is not uniform throughout its total area. In fatliquoring or stuffing operations, the more porous parts take up more lubricants than those less porous. Consequently, the amount of grease (and of *p*-nitrophenol incorporated with the grease) in different locations of the hide will vary. Table 1 shows the magnitude of this variability found by analyses at the National Bureau of Standards. Samples were cut from six different sampling locations of two sides (half hides) of Army retan upper leather from

TABLE I

Distribution of Grease and *p*-Nitrophenol over Area of Sides of Army Retan Upper Leather

	Sampling positions					
	1		4		7	
Side	Grease	*p*-Nitrophenol	Grease	*p*-Nitrophenol	Grease	*p*-Nitrophenol
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
1	24.5	0.20	23.2	0.20	20.9	0.21
2	28.2	0.24	24.2	0.22	23.2	0.23
	13		22		26	
1	23.1	0.22	30.8	0.23	31.7	0.26
2	23.7	0.20	27.0	0.23	32.6	0.30

Variability	High	Low	Average
Grease, Per cent	32.6	20.9	26.2
p-Nitrophenol, Per cent	0.30	0.20	0.23

one tannery. The sampling locations are designated by the numbering system employed in the sampling study reported by Mann[17] and were chosen to represent areas with different fiber structures so that a proper evaluation of the side as a whole could be obtained. It is seen that the *p*-nitrophenol concentration varies only about 0.1 per cent over the area of a side. This variability is not serious, as it is of the same magnitude as the specification tolerance.

(b) *Retreatment of Finished Items*

Since *p*-nitrophenol is somewhat soluble in water, the mildewproofness of leathers treated with it will be lost when exposed to leaching. Retreatment of footwear that has been in use for some time is necessary for further protection. For military shoes and boots, an emulsion type of *p*-nitrophenol formulation is used by the Army. The composition of the formulation follows:

p-Nitrophenol Retreatment Formulation

Emulsion	
5%	*p*-nitrophenol
95%	sulfonated cod or neat'sfoot oil
1	part of this mixture diluted with 5 parts water to give an emulsion containing 0.8% *p*-nitrophenol

FIGURE 1.—Appearance after storage for 6 months in the tropical room. Boot free from mildew had been treated with *p*-nitrophenol. The other boot contained no fungicide.

Retreatments consist of immersing the boots or shoes in the formulation for 10 minutes. Figure 1 shows a pair of shoes that had been stored under conditions very favorable to mildew growth in a tropical room at the U. S. Army Engineering Center, Fort Belvoir, Virginia. The shoe without mildew growth had been treated, while the other had received no treatment.

3.3 *Development of New Leather Mildew - Preventives*

Though *p*-nitrophenol is the preferred leather fungicide at the present time, search for additional fungicides continues in an effort to find alternate compounds that are as good or better than *p*-nitrophenol.

During the past several years, a number of compounds have been investigated at the National Bureau of Standards in a screening program supported by the Office of The Quartermaster General. Nearly all of these compounds had shown fungistatic activity in tests on substrates other than leather. At the National Bureau of Standards, these compounds were first subjected to what is designated as the initial screening test for leather fungicides.

(a) *Initial Screening Test*

Vegetable-tanned leather samples were treated with organic solvent-type formulations of the compound so as to contain about 0.6, 0.3, and 0.15 per cent of the compounds. These samples, some specimens of which were tumbled in water after the treatments, were then tested for mildew resistance by ex-

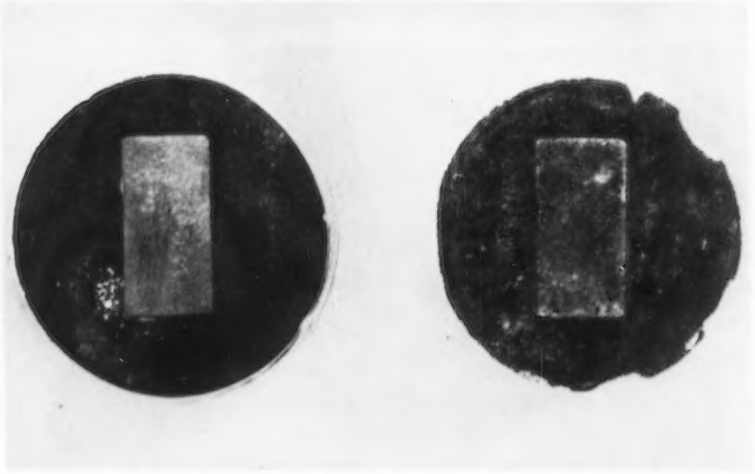


FIGURE 2.—Initial screening test.
Left: Mildewproofed leather sample.
Right: Untreated leather sample.

posure on mycelial mats of *A. niger* (ATCC-6275) growing on nutrient agar plates incubated at 29°C, for seven days. Figure 2 illustrates the samples and their method of exposure.

If none of the samples were mildewproof in this test, the compound was considered to have failed as a leather mildew-preventive and was tested no further. (*p*-Nitrophenol prevents mildew growth in this test at 0.15 per cent concentration.) If mildew was found on none of the samples, or only on the samples containing 0.3 per cent or less of the fungicide, it was subjected to a more severe test, which is referred to as the tropical-room-exposure test.

(b) *Exposure in Tropical Room*

Leather samples treated as in the initial screening test were exposed in a tropical room at Fort Belvoir, Virginia. These test samples are illustrated by fig. 3. This room, used by permission of the Office of The Chief of Engineers, U. S. Department of the Army, is maintained at temperatures and humidities simulating as nearly as possible those experienced in the tropics. The samples were inspected for mildew growth weekly for five weeks after storage. (Mildewproofness is obtained in this test by 0.3 per cent *p*-nitrophenol, while untreated samples are covered with mildew in two weeks.)

(c) *Other Tests*

In addition to tests for fungistatic activity, observations were also made on other characteristics that have a bearing on the usefulness of the fungicide as a leather preservative, such as:

Corrosiveness to metal parts.
Stability to heat and light.
Solubility.

A good leather mildew-preventive should be resistant to leaching, that is, it should not be very water-soluble, but should be readily soluble in suitable organic solvents and compatible with leather grease.

(d) *Results of Tests*

From the compounds that have been tested by the screening program described, several have been found that will prevent mildew growth on leathers at about the same concentrations as *p*-nitrophenol. With a few exceptions these are other phenol derivatives. None has been found that is markedly superior to *p*-nitrophenol in leather mildew-preventive efficiency, though several effective ones may be better from the standpoint of color and permanency. At the present time, some of the more promising fungicides tested are being studied further under field conditions by the Quartermaster Corps.

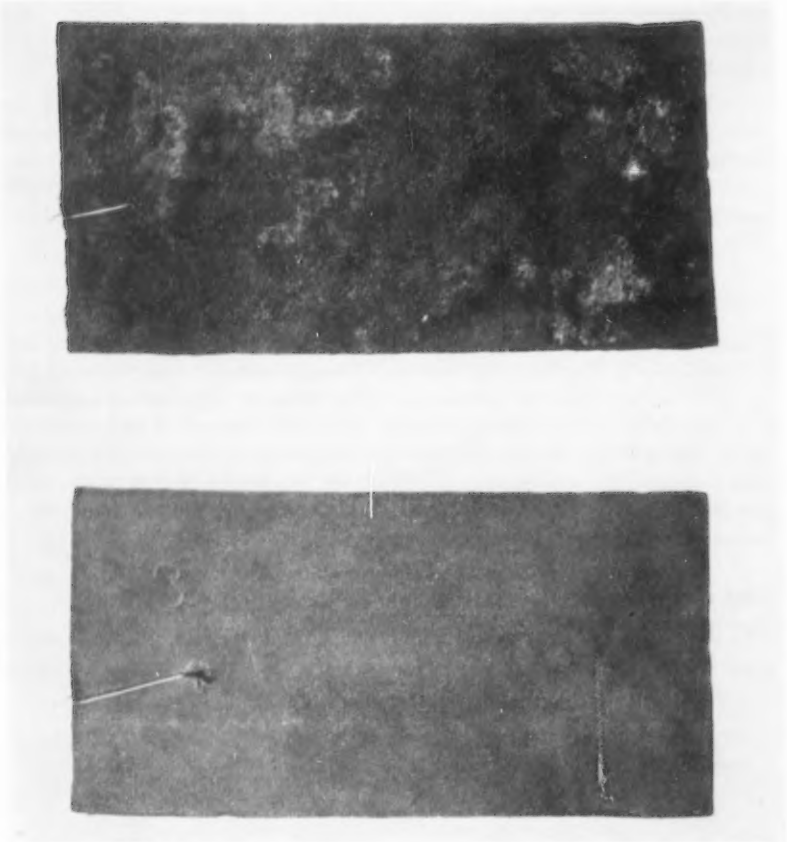


FIGURE 3.—Tropical-room-exposure test.
Top: Untreated leather sample.
Bottom: Same leather that had been mildewproofed by treatment with a fungicide.

An ideal leather fungicide has not yet been found. Such a compound should have the following properties: It should be cheap, colorless, easy to apply, harmless to human health and to leather, and should give effective and permanent mildew protection.

3.4 *Relationship between Fungistatic Activity and Chemical Structure*

Studies on this subject involving chlorinated phenols and nitrophenols have been made by Shirk and coworkers[20,21] using pure cultures and nutrient

agar test medium. Usually, the relationship found in such studies may be expected to prevail when applied to leather. Exceptions to this, however, should not be surprising. Besides the differential response of microorganisms due to the substrate, unknown alterations in the fungicide structure may occur by reactions with other formulation components or with the leather. Furthermore, in the tropical-room-exposure test, the fungicide concentration in the leather may decrease by leaching due to repeated condensations in the humid atmosphere. The relative water solubilities of the fungicides may, therefore, be a factor in the determination of their mildew-preventive efficiencies in this test.

A good leather mildew-preventive will probably show high fungistatic potency against *A. niger* when added to nutrient agar medium. It does not follow, however, that all fungicides with high potency in the agar test or on other substrates, such as paint or textiles, are good leather mildew-preventives.

Hausam [6] recently studied the effect of number and position of the chlorine atoms in chlorinated phenols, cresols, and xylenols on disinfecting powers of these compounds in aqueous media when used as preservatives for skin and leather. In his study and that of Shirk, previously referred to, inhibition of activity was found to be especially associated with substitution in the para position by chlorine.

The National Bureau of Standards has not made a systematic study on the effect of chemical structure on leather mildew-preventive potency. From the screening program that has been described, however, a few comparisons are possible which are shown in tables 2-5.

The percentages shown in parentheses in tables 2-5 are the lowest concentrations that produced mildewproof leathers in the tropical-room exposure test.

Though compounds of many types have been tested, phenols predominate as the type found most effective as leather mildew-preventives, and particularly the 4-nitro and 4-thiocyanophenols. Possibly these compounds are effective because they can combine with the leather by hydrogen bonding. The inefficiency of *o*-nitrophenol, which is intramolecularly hydrogen-bonded, seems to fit this hypothesis. That *p*-nitrophenol is really fixed in the leather was recently demonstrated by the observation at the National Bureau of Standards that this fungicide could not be extracted with chloroform from some types of leathers unless the leather samples were first wetted with water. The chloroform extraction is utilized in the specification analysis for *p*-nitrophenol. Apparently fixation of the *p*-nitrophenol to reactive groups in the leather occurs, but it is released when the reactive groups are satisfied with water. This probably involves a hydrogen-bonding mechanism.

TABLE 2

The Relative Efficiencies of Some Nitrophenols as Leather Mildew-Preventives

Compound	Efficiency
p-Nitrophenol	High (0.3 per cent)
Ortho-chloro-*p*-nitrophenol	Very high (0.15) per cent)
3,5-Dimethyl-*p*-nitrophenol	Quite high (0.6 per cent)
Ortho-nitrophenol	Low (greater than 1.0 per cent)

TABLE 3

The Relative Efficiencies of Some 4-Thiocyanophenols

Compound	Efficiency
4-Thiocyanophenol	Very high (0.15 per cent)
4-Thiocyano-*o*-cresol	High (0.30 per cent)
4-Thiocyano-3, 5-xylenol	Quite high (0.6 per cent)
3-Ethyl-4-thiocyanophenol	Quite high (0.6 per cent)
4-Thiocyano-2,6-xylenol	Moderate (greater than 0.6 per cent)

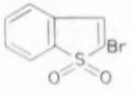
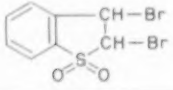
TABLE 4

The Relative Effects of Substituents in the Para Position of Phenols

Compound	Efficiency
3,5-Dimethyl-*p*-nitrophenol	Quite high (0.6 per cent)
3,5-Dimethyl-*p*-thiocyanophenol	Quite high (0.6 per cent)
3-5-Dimethyl-*p*-chlorophenol	Moderate (greater than 0.6 per cent)

Table 5

Sulfones

Compound	Efficiency
2-Bromothianaphthene-1-dioxide	High (0.3 per cent)
	
2,3-Dibromo-2,3-dihydrothia-naphthene-1-dioxide	Moderate (greater than 0.6 per cent)
	

Alkylation of *p*-nitrophenols and *p*-thiocyanophenols seems to decrease slightly the mildew-preventive efficiency of the compounds, while chlorination (in the case of *o*-chloro-*p*-nitrophenol, table 2) seems to increase the efficiency.

2-Bromothianaphthene-1-dioxide differs structurally from 2,3-dibromo-2, 3-dihydrothianaphthene-1-dioxide only in that the former has an ethylenic linkage, which, in the latter, has been saturated by the addition of hydrogen bromide. Apparently the ethylenic linkage in the former case is associated with higher mildew-preventive efficiency. No explanation for these observations can be offered at this time.

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Laboratory and Field Exposure Studies of Leather Fungicides†

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ABSTRACT

The effectiveness of seven experimental leather fungicides that were previously evaluated in laboratory tests has been studied under field conditions together with 4-nitrophenol as the comparison standard. In addition to 4-nitrophenol, it was found that 2-chloro-4-nitrophenol, 4-thiocyanophenol, and bis(4-nitrophenyl) carbonate prevent mildew growth on leathers under tropical jungle conditions at concentrations no higher than 0.60 per cent and are adequately stable under severe weathering conditions. N-(trichloromethylthio) tetrahydrophthalimide and tetrachlorohydroquinone inhibited mildew growth at 0.60 per cent concentration in some cases, but are not dependable leather fungicides. 2-Phenylphenol and 4-chloro-m-xylenol are not effective leather fungicides even at concentrations well over one per cent.

1. INTRODUCTION

Prevention of mildew growth on military leather items has been an important problem for the United States Armed Forces since World War II. Most tanning agents and leather lubricants required for the production of satisfactory military leathers are mildew susceptible. It is, therefore, necessary to incorporate a fungicide* into the leather to make it mildew resistant in hot and humid areas. The fungicide now being used for that purpose by the Quartermaster Corps is 4-nitrophenol. A comprehensive review on the use of this compound as a leather fungicide has recently appeared in the literature. [1]

†These studies were sponsored by the Quartermaster Corps of the Department of the Army as a part of research and development project 7-65-01-004R.
*Throughout this paper the term fungicide is applied to any compound that prevents or inhibits mildew growth.

Although 4-nitrophenol is the preferred leather fungicide at the present time, new and possibly better ones are being sought. In time of national emergency any one fungicide might be unavailable. This was true of 4-nitrophenol during World War II. The availability of suitable alternates is consequently required.

The Quartermaster Corps is supporting a program at the National Bureau of Standards for the investigation of compounds that are known to be fungitoxic* and that might be useful as leather fungicides. Part of this program has consisted of screening numerous compounds in order to determine those most effective in inhibiting mildew growth in leather.

A field exposure study of some of the compounds evaluated in screening tests was undertaken for two reasons: (1) in order to test further the weathering stability and fungicidal efficiency of those compounds that had been found promising in the earlier screening tests, and (2) in order to establish the reliability of the screening test as a method for predicting the efficiency of fungicides in field tests.

2. Description of the QMC Screening Program for Leather Fungicides at NBS

As previously mentioned, all the compounds that have been submitted for evaluation as leather fungicides at the National Bureau of Standards possessed fungitoxic properties. This was known from fungitoxicity tests, such as that employed by the Prevention of Deterioration Center of the National Research Council [2], or the fact that the compounds had already been used as fungicides for protection of materials other than leather.

It is generally recognized that the fungitoxicity exhibited by a given compound against a specific organism is greatly influenced by the substrate and by other environmental factors [3]. Leather is a complex material that supports the growth of a great variety of organisms, most of which have been studied to only a limited extent. Compounds that are found to be effective fungicides for other materials, such as textiles or paints, or that exhibit fungicidal activity in tests using pure cultures and nutrient agar medium are not necessarily good leather fungicides. From these considerations it is obviously desirable to evaluate leather fungicides on a leather substrate and preferably under the conditions and against microflora typical of a tropical jungle. Such conditions and flora are approximated in a tropical room at the Engineering Center of the U. S. Army at Fort Belvoir, Virginia. This room, which is referred to only as the tropical room in the remainder of this paper, was made available for use in the Quartermaster Corps screening program of leather fungicides at the National Bureau of Standards through the cooperation of the Engineering Center. Some details of the procedures used in the screening program are given as a background for the present field exposure study.

*No attempt has been made to distinguish between fungicidal and fungistatic activity.

2.1 *Test Leather*

After evaluating the fungus resistance of different leathers by exposure in the tropical room, a vegetable-tanned sole leather crust was chosen as the test leather. This leather contains less filler and oil than finished sole leather and is not compressed by rolling. It is very susceptible to mildew growth and is uniformly so from batch to batch. Many other types of vegetable-tanned leathers vary considerably in this respect. Vegetable-tanned leathers are more susceptible to mildew growth than leathers of other types of tannages [3].

2.2 *Incorporation of Fungicides into the Leather*

Leather specimens were dipped into a suitable organic solvent-type formulation of the fungicide. The choice of solvents apparently does not affect the fungitoxic properties of the compound. This conclusion has been reported by others [4] and assumes no reaction between solvent and fungicide. Whenever possible, a solvent mixture of cyclohexanone (10 per cent), mineral oil (20 per cent), and trichloroethylene (65–70 per cent according to per cent fungicide, by weight) was used for incorporation of the fungicide into the test leather. This mixture penetrates quickly through the leather. Analysis of leather treated with 4-nitrophenol in this solvent mixture indicated that the deposition of the fungicide was uniform throughout the leather. The amount of fungicide deposited, as found by analysis, agreed generally with the amount calculated from the formulation absorption by the leather. Apparently, there is no preferential absorption of the components of the formulation.

2.3 *Tests for Mildew Resistance*

(a) *Initial screening test*

Fungicides submitted for test were exposed to an initial screening test as follows: The fungicide was dissolved in an organic solvent such as trichloroethylene, cyclohexanone, Stoddard solvent, or combinations of these. The solution was then applied to 2- by 4-inch vegetable-tanned sole leather specimens by immersing the leather in the solution. The pickup of fungicide was determined by differences in weight before and after immersion. The specimens were dried for a minimum of 24 hours and cut into four specimens 1 inch by 2 inches.

Testing was done according to Federal Specification KK-L-311a, Leather; Methods of Sampling and Testing, Methods 5011 and 5021, as follows: Mycelial mats were prepared by suspending the spores of a ripe, fruiting agar culture of *Aspergillus niger* (ATCC-6275) in 100 ml. of distilled water containing a small amount of wetting agent. Using a sterile camel's hair brush, the spore suspension was brushed uniformly over the surface of a hardened, sterile nutrient agar medium. Prior to inoculation, the culture medium was

sterilized in an autoclave for 20 minutes at 122°C., poured into sterile 3-inch Petri dishes under aseptic conditions and allowed to harden. After inoculation, the Petri dishes were incubated for approximately 48 hours at 29°C., relative humidity 85–90 per cent. At the end of the incubation period, the surface of the agar medium was covered with a white mycelial mat of the test organism.

Two of the 1- by 2-inch leather specimens were tumbled for three hours in shake bottles containing distilled water. These specimens plus a third non-tumbled specimen were placed on the mycelial mats of *A. niger*. The specimens were incubated for seven days at 29°C. at a relative humidity of 85 to 90 percent. A leather specimen free of fungicides was exposed concurrently as a control. If the control failed to show a heavy growth of mildew the test was repeated. The results of the test were determined by visual examination of the specimens.

Other specimens were tested for resistance to mildew growth by the American Leather Chemists' Association sand spore mixture. These specimens were incubated for 21 days under the same conditions described previously. Visual examination for mildew growth was made on the seventh, fourteenth, and twenty-first day of the incubation period.

(b) *Second stage screening test or tropical room exposure test*

Fungicides that were found to prevent or to a considerable extent inhibit mildew growth in the initial screening test were tested further by the tropical room exposure test. Leather specimens containing definite percentages of the fungicides were exposed for five weeks in the tropical room. The specimens were inspected for mildew growth once each week. In many cases a treatment that made the test leather mildew-proof in the initial screening test failed even to inhibit mildew growth in the tropical room exposure; no treatment shown to be ineffective by the initial screening test has been found effective by the tropical room test. Treatments that merely inhibit mildew growth in the initial screening test are always less effective in the tropical room exposure. Tropical room exposure appears to be a more severe test for leather fungicides.

The minimum percentage of a given fungicide required to make the test leather mildew resistant in the tropical room exposure test is assumed to be the percentage required for protection under the most severe conditions military leather items will encounter during service. 4-Nitrophenol, present in the leather at 0.3 per cent concentration, prevents mildew growth under the tropical room conditions. Generally, no higher concentration than 0.6 per cent has been used in the screening program since the search has been directed towards finding fungicides as effective as or more effective than 4-nitro-

phenol. If a compound did not exhibit at least some inhibition of mildew growth at 0.6 per cent, it was considered too ineffective to be of value. Others were unsuitable as leather fungicides because of obvious defects from the standpoint of color, stability, and solubility characteristics, or were known to possess properties considered harmful to human health. Consequently, only a few compounds out of those screened to date can be considered as substitutes or alternates for 4-nitrophenol as a leather fungicide in Quartermaster items. The more promising ones found in the screening program are reported upon in this paper.

3. Field Exposure Study

3.1 *Compounds*

Eight fungicides were included in the field exposure study. All of these had prevented or greatly inhibited mildew growth at no more than 0.3 per cent in the initial screening test described in 2.3 (a). One of the fungicides was 4-nitrophenol, which was used as the comparison standard. The fungicides and their relative mildew-preventive efficiencies as found in the tropical room screening test described in 2.3 (b) are listed in table 1. The borderline concentrations referred to in the table are the minimum percentages of the fungicides required in the leather to make it mildew resistant under the tropical room conditions. With two exceptions, the fungicides prevented or greatly inhibited mildew growth at no more than 0.3 per cent as shown in table 1. A concentration of 0.6 per cent of 2-phenylphenol or 4-chloro-m-xylenol was

TABLE 1

Screening Test Results (Tropical Room) of Fungicides used in Field Exposure Study

Fungicide No.	Name	Borderline concentration Per Cent
1	4-thiocyanophenol	0.15
2	2-chloro-4-nitrophenol	0.15
3	4-nitrophenol (comparison standard)	0.30
4	bis(4-nitrophenyl) carbonate	0.30
5	tetrachlorohydroquinone	0.30
6	N-(trichloromethylthio) tetrahydrophthalimide	0.30*
7	2-phenylphenol	0.60**
8	4-chloro-m-xylenol	0.60***

*Leather specimens containing 0.15 per cent of the fungicide were mildew resistant if the specimens had not been exposed to heat or light. Specimens heated for 1 week at 80° C. or exposed to sunlight for 1 week were not completely mildew resistant even when containing 0.60 per cent of the fungicide. A concentration of 0.30 per cent was taken as the borderline concentration for storage conditions.

**0.60 per cent did not prevent mildew growth. Nearly total inhibition of mildew growth required a minimum of 1.5 per cent deposition in subsequent tests.

***0.60 per cent did not prevent mildew growth. This compound was not tested at concentrations greater than 0.60 per cent.

not sufficient to prevent mildew growth. Subsequent testing has shown that a minimum concentration of 1.5 per cent of 2-phenylphenol was required for nearly total inhibition of mildew growth in the tropical room screening test. 4-Chloro-m-xylenol was not tested at concentrations greater than 0.6 per cent. Leather specimens containing 0.15 per cent of N-(trichloromethylthio) tetrahydrophthalimide were mildew resistant in the tropical room screening test if the specimens had not been exposed to heat or light. Specimens heated for one week at 80°C. or exposed to direct sunlight for a week were not completely mildew resistant even when containing 0.6 per cent of this fungicide.

2-Phenylphenol and 4-chloro-m-xylenol were included in the present study even though they had been found comparatively ineffective in the tropical room screening test. The resons for this were: (1) to permit comparison of field exposure results and screening test results on some relatively ineffective fungicides as well as on relatively effective ones, and (2) because price and availability were thought to be factors potentially favorable to these fungicides if they were effective at higher concentrations than had been used in the screening tests. However, most of the compounds listed are not yet commercially available and no complete comparison as to cost can be made at this time. The National Bureau of Standards has not investigated methods of tannery applications and has not made tests for properties relating to human health hazards of any of the fungicides included in this study.

3.2 *Preparation of Leather Samples*

Three types of leathers were used in this study and are referred to as leathers A, B, and C:

A—Vegetable-tanned sole leather crust. This is the same type of leather that had been used in the screening test described previously.

B—Vegetable-tanned strap leather.

C—Chrome-retanned military-type upper leather.

All of these leathers were obtained free of 4-nitrophenol or any other fungicide. Four bends of leather A, four sides (half hides) of leather B, and two hides of leather C were used. Four like sets of leather samples were prepared, one each for the four exposure sites used (see section 3.6). Each of the eight fungicides was tested at three concentration levels, and three specimens of each type leather were used for each level. In addition, three controls (specimens containing no fungicide) of each type leather were included in each set of samples. The total number of specimens sent to each exposure site was therefore 225, and this amount constituted one set of samples. The size of each specimen was 2 by 4 inches. Only those portions of the bends, sides, or hides that were free from obvious flaws, such as scars and creases, were used. All specimens of each leather were cut out, mixed, and assigned to

fungicide treatments and to set of samples at random, and marked for identification.

3.3 *Formulations*

A 5-per cent (by weight) organic solvent stock formulation of each fungicide was first prepared. Portions of the stock formulation were then diluted to the concentrations required to deposit the desired percentage of fungicide in the leather. All dilutions of the stock formulation of a given fungicide were made with the same solvent mixture as was used in that stock formulation, with the exception of the formulation of 2-phenylphenol (see (d), this section).

The formulation compositions were as follows:

(a) *For 4-thiocyanophenol, 2-chloro-4-nitrophenol, 4-nitrophenol, and 4-chloro-m-xylenol*: 10 per cent cyclohexanone, 20 per cent mineral oil, and trichloroethylene to make to 100 per cent.

(b) *For bis(4-nitrophenyl) carbonate and N-(trichloromethylthio) tetrahydrophthalimide*: 50 per cent dioxane, 10 per cent neat's-foot oil, and chloroform to make to 100 per cent.

(c) *For tetrachlorohydroquinone*: 30 per cent cyclohexanone, 20 per cent mineral oil, and trichloroethylene to make to 100 per cent.

(d) *For 2-phenylphenol*: A 5-per cent formulation of this compound was supplied by the manufacturer and used as supplied for the treatment of all specimens receiving the highest concentration of 2-phenylphenol. For the treatment of specimens receiving lower concentrations, the 5 per cent formulation was diluted with the solvent mixture shown under (a).

3.4 *Concentration Levels of the Fungicides in the Leather*

As has been mentioned, each fungicide was tested at three levels of concentration. (a) When the approximate borderline concentration had been established in screening tests (see the table in section 3.1), the three levels were: *Highest level*: Twice the borderline concentration; *Intermediate level*: Borderline concentration; *Lowest level*: One-half the borderline concentration. (b) For 2-phenylphenol and 4-chloro-m-xylenol where the borderline concentrations had not been established in screening tests, the three levels were: *Highest level*: For 2-phenylphenol, the per cent deposition obtained by treatment of the leathers with the 5-per cent formulation supplied by the manufacturer was used. For leathers A, B, and C these depositions became, respectively, 1.5 per cent, 1.7 per cent, and 1.1 per cent, corresponding to differences in absorptivity of the leathers. For 4-chloro-m-xylenol, 1.2 per cent was used, or twice the highest concentration used in the previous screening tests: *Intermediate level*: 0.60 per cent; *Lowest level*: 0.30 per cent.

3.5 *Treatment of Leather Specimens*

The leather specimens were treated by dipping into formulations of the required concentrations to give the desired per cent depositions of the fungicides in the leather. The required formulation concentrations were calculated from the average per cent of the formulation absorbed by the respective leathers during the treatment, determined in preliminary experiments. The calculated per cent depositions of the fungicides in the leathers were checked by analyses in the cases of 4-nitrophenol, tetrachlorohydroquinone, and 2-phenylphenol, for which analytical methods were available [5, 6, 7]. The agreement between the calculated fungicide percentages and those found by analyses was of the order that could be expected from the variability in formulation absorption by individual specimens. This variability is shown in the following table.

Leather	No. of specimens tested	Formulation absorption	
		Average	Range*
		Per cent	Per cent
A	24	45.0	15.9
B	24	53.0	11.7
C	24	38.0	14.8

*Largest minus smallest.

All specimens of one leather receiving the same treatment were treated simultaneously. The controls (specimens containing no fungicide) were treated with the solvent mixture described in (a), section 3.3. After treatment, the specimens were placed in an oven at 80°C. for 6 hours in order to remove the volatile solvents.

3.6 *Exposure Conditions*

Four like sets of leather samples, prepared and treated as described, were exposed as follows:

Sample set 1—Exposed at Yuma, Arizona (desert weathering, hot-dry environment). The samples were exposed to direct sunlight but were sheltered from desert storms. They were reversed twice during the exposure period so that grain and flesh surfaces received about equal amounts of sunlight. The exposure lasted for three months (from July 6 to October 6, 1954) and the samples were subsequently tested for mildew resistance by storage in the tropical room at Fort Belvoir, Virginia.

Sample set 2—Exposed on a roof at the National Bureau of Standards, Washington, D. C. (weathering, moderate hot-dry environment). The samples were exposed in the open during working hours, but sheltered the rest of the

time and during rainstorms. Grain and flesh surfaces received about equal sunlight exposure. The exposure period and subsequent mildew-resistance test were the same as described for sample set 1.

Sample set 3—Not exposed to weathering. The samples were stored in the laboratory and were not exposed to any direct weathering before they were tested for mildew resistance by exposure in the tropical room.

Sample set 4—Exposed in Panama (mildew-growing conditions, hot-humid environment). The samples were protected from direct sunlight and rain, but were otherwise exposed to an ambient environment at a site located in the jungle on the Atlantic side of the Isthmus of Panama. Weekly observations of mildew growth on these samples were made for a period of 12 weeks (from August 3 to October 25, 1954) after growth began to appear on some specimens. Previous to this period, the samples had been exposed at two other Panama sites for a total of five weeks, during which time no mildew growth appeared even on untreated specimens. The environmental conditions at the first two sites apparently were unsuitable for rapid mildew growth and made relocation necessary. Summaries of the climatological data collected at the various exposure sites, and the daily cycle of temperature and per cent relative humidity of the tropical room, are given in an appendix to this paper, although no discussion of the effect of the climatological conditions on mildew growth is included in this study.

It may be observed that none of the exposure conditions was such that specific information about the effect of leaching by water on the permanency of the fungicidal treatments could be obtained. However, both in the Panama exposure and in the tropical room exposure the samples were wetted to the point of dripping during repeated condensations of the humid atmospheres. Some leaching effect is, therefore, considered to be included in the over-all effectiveness of the fungicides under these conditions.

All four sets of samples were prepared during the first part of May 1954 and sent to the various exposure sites during the following month. The samples exposed at Yuma, Ariz., (sample set 1) were returned to the National Bureau of Standards about the middle of October 1954, and sets 1, 2, and 3 were then tested for mildew resistance in the tropical room simultaneously.

The exposures of the samples at Yuma, Ariz., and in Panama as well as the observations on mildew growth on the latter samples were conducted by the Quartermaster Research and Development Field Evaluation Agency, Fort Lee, Virginia.

3.7 *Collection and Treatment of Test Data on Mildew Growth*

Weekly observations on mildew growth were made and recorded separately for the grain and flesh areas and the edges of each specimen. The amount of mildew growth was indicated by the percentage of the given area covered with it and was designated by the following code numbers:

0—No mildew growth.

1—From scattered colonies to 25 per cent of the area covered with mildew growth.

2—From 26 per cent to 50 per cent of the area covered with mildew growth.

3—From 51 per cent to 75 per cent of the area covered with mildew growth.

4—From 76 per cent to 100 per cent of the area covered with mildew growth.

The treatment of the original test data to obtain the data shown in figures 1 - 4 was performed as follows:

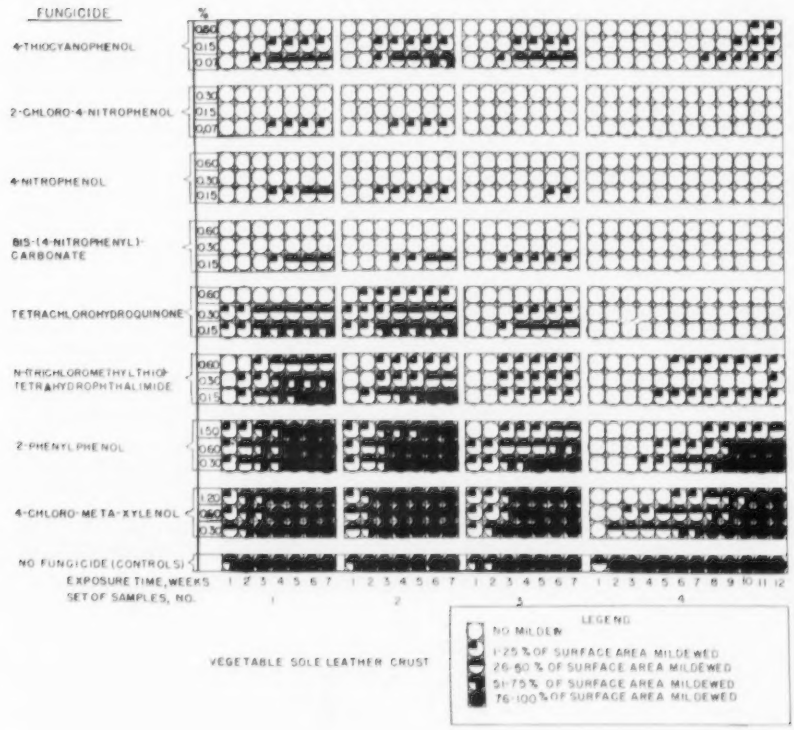

FIGURE 1.—Weekly observations on mildew growth on vegetable-tanned sole leather crust.

Sample set 1 was exposed to weathering at Yuma, Ariz.
Sample set 2 was exposed to weathering on NBS roof.
Sample set 3 was not exposed to weathering (stored in NBS lab.)
These samples were tested for mildew resistance by exposure in a tropical room.
Sample set 4 was not exposed to weathering prior to being tested for mildew resistance by exposure at a Panama jungle site.

(a) *Derivation of a single value for each specimen*

If the values recorded for grain and flesh on a given specimen were the same, that value was taken as the value for the specimen. If they were not the same, the higher value was taken as the specimen value rather than the average. It is assumed that mildew growth is equally objectionable whether it grows on grain or flesh. If a fungicide does not give the same protection to both sides of the leather, it should be rated according to the area on which it is least effective.

Mildew growth on the edges was neglected. The sizes of edge areas are negligible compared to grain or flesh areas. Furthermore, the cut and loose

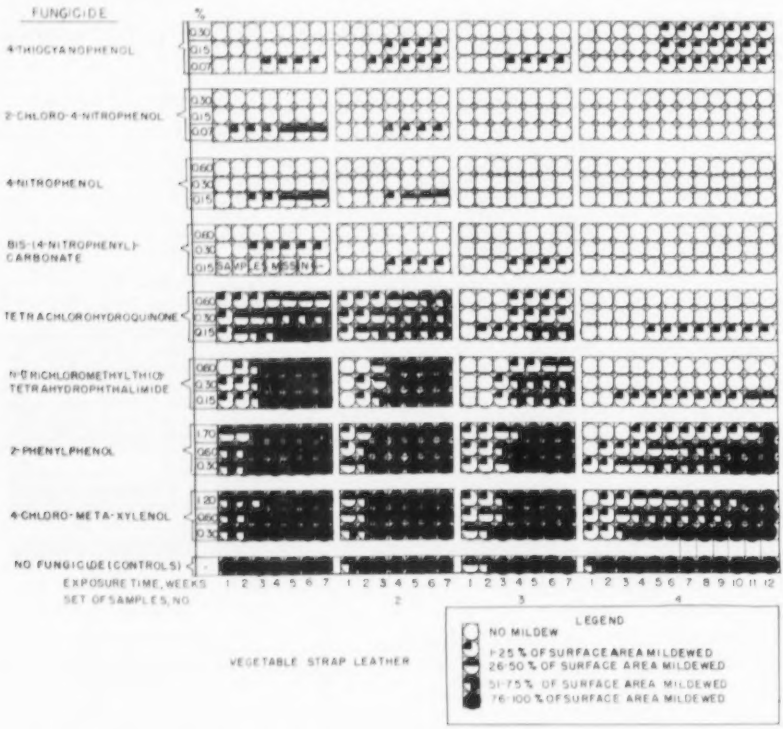

FIGURE 2.—Weekly observations on mildew growth on vegetable-tanned strap leather.
Sample set 1 was exposed to weathering at Yuma, Ariz.
Sample set 2 was exposed to weathering on NBS roof.
Sample set 3 was not exposed to weathering (stored in NBS lab.).
These samples were tested for mildew resistance by exposure in a tropical room.
Sample set 4 was not exposed to weathering prior to being tested for mildew resistance by exposure at a Panama jungle site.

fibers of edge areas are not typical of the surfaces that are of most concern in leather mildew prevention.

(b) *Derivation of a single value for each treatment*

After a single value for each of the three specimens receiving the same treatment was obtained as explained in (a), the average of the three values was taken as the mildew growth for that treatment. This average was rounded off to the nearest whole number.

3.8 *Results*

Figures 1, 2, and 3 are graphs of all data on observations of mildew growth

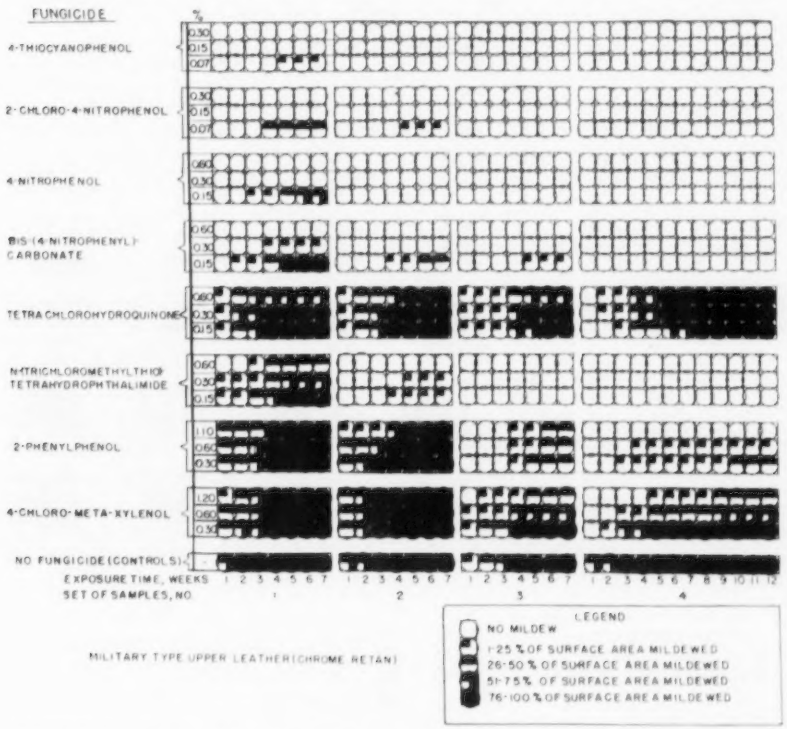

FIGURE 3.—Weekly observations on mildew growth on chrome-retanned military-type upper leather.

Sample set 1 was exposed to weathering at Yuma, Ariz.

Sample set 2 was exposed to weathering on NBS roof.

Sample set 3 was not exposed to weathering (stored in NBS lab.).

These samples were tested for mildew resistance by exposure in a tropical room.

Sample set 4 was not exposed to weathering prior to being tested for mildew resistance by exposure at a Panama jungle site.

after the original data have been treated as described in section 3.7; they show the results for sole leather crust, vegetable strap leather, and military-type upper leather, respectively. Weekly accumulations of mildew growth on leathers containing the various concentrations of each of the eight fungi-

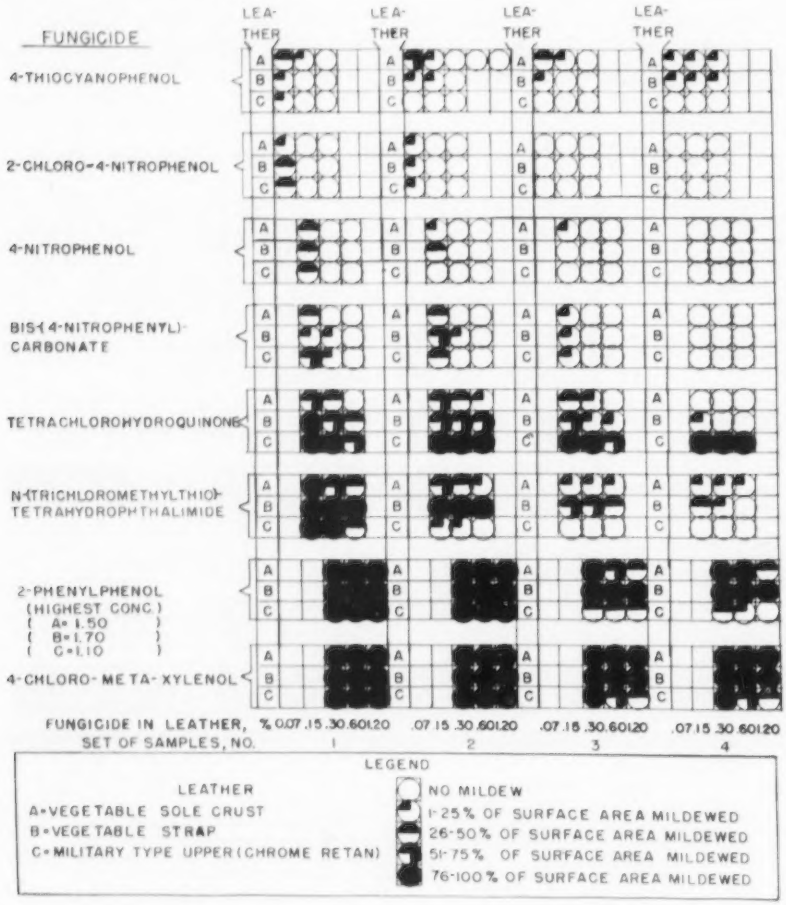

FIGURE 4.—Final mildew growth on leather after completion of mildew resistance tests.
Sample set 1 was exposed to weathering at Yuma, Ariz.
Sample set 2 was exposed to weathering on NBS roof.
Sample set 3 was not exposed to weathering (stored in NBS lab.).
These samples were tested for mildew resistance by exposure in a tropical room.
Sample set 4 was not exposed to weathering prior to being tested for mildew resistance by exposure at a Panama jungle site.

cides are shown. The tropical room exposure was terminated after five weeks. The Panama exposure was terminated after 12 weeks at the final exposure site. Figure 4 is a compilation of information taken from figures 1, 2, and 3; it shows the final accumulations of mildew growth on all leathers of the four sets of samples after completion of the mildew-resistance tests.

3.9 *Discussion*

(a) *Tropical room exposure versus Panama exposure*

Examination of the data for the two sets of samples not exposed to weathering prior to the mildew growth exposure (sample sets 3 and 4) shows that initial mildew growth generally appeared on corresponding specimens after shorter exposure times in the tropical room than at the Panama site (figures 1, 2, and 3). This is to be expected since the tropical room is controlled so as to produce continuous optimum conditions for mildew growth, while at the Panama site natural atmospheric conditions prevailed. The latter conditions were not uniformly optimum for mildew growth. Figure 4 shows that the two sets of samples yielded final data that are in good agreement, except those for tetrachlorohydroquinone in leathers A and B. However, there are clear indications that a 5-week exposure period in the tropical room is at least as severe a test for mildew resistance as a 12-week exposure period at the Panama jungle site.

(b) *Effect of weathering*

Comparison of the three sets of samples exposed to mildew growth in the tropical room, but previously exposed to different weathering conditions (sample sets 1, 2, and 3), shows that weathering appears to make the leathers more susceptible to mildew growth. From figures 1, 2, and 3 it is seen that mildew generally appeared first on weathered samples. This difference is persistently reflected in the final data also, as may be observed from figure 4. The greater mildew susceptibility of weathered samples may be due to greater accumulation of dirt and spores on them compared to samples that were stored in the laboratory. It may also be due to fungicide removal or degradation caused by weathering.

The results of this study show no appreciable differences among the fungicides in sensitivity to weathering. In the screening test evaluation (see the table in section 3.1), N-(trichloromethylthio)tetrahydrophthalimide exhibited fungicidal effectiveness when leather specimens containing it were not exposed to heat or light, and decreased effectiveness after exposure to these conditions. In the field exposure study the instability of this fungicide when exposed to heat and light (weathering) was not so marked. Possibly the long storage period of the unweathered treated samples (about 6 months) before they were tested for mildew resistance had an effect similar to direct weather-

ing and so obscured the characteristics observed in the screening tests. In the screening tests the samples were tested for mildew resistance within about one month after treatment.

There is no appreciable difference in mildew resistance between the samples exposed to weathering at Yuma, Ariz., and those exposed on a roof at the National Bureau of Standards, Washington, D. C. There was, however, a surprising contrast between the two exposures in their effects on the color of the two vegetable-tanned leathers. The Yuma exposure of these leathers made them lighter in color than they were originally, while the NBS roof exposure made them darker. The explanation for this phenomenon presumably is associated with differences in atmospheric conditions at the two locations. During the exposure in the tropical room, the color differences between the two sets of samples disappeared.

Both weathering exposures produced stiffening and curling of the leather specimens. Vegetable strap leather was affected the most in these respects and military upper leather with high grease content was affected the least. The stiffening and curling were more marked on the samples exposed at Yuma than on those exposed at NBS.

(c) *Relative effectiveness of the fungicides used in this investigation*

The following ranking according to decreasing effectiveness is derived from the over-all results shown in figure 4.

(1) 2-Chloro-4-nitrophenol: No more than 0.15 per cent was required to make all leathers of all sets of samples mildew resistant. This fungicide appears to be slightly more effective than 4-nitrophenol and is the only one of those investigated that is ranked more effective than 4-nitrophenol.

(2) 4-Thiocyanophenol and 4-nitrophenol: No more than 0.30 per cent was required to make all leathers of all sets of samples mildew resistant except for a very slight amount of mildew found on leathers A and B, Panama samples, that contained 0.30 per cent of 4-thiocyanophenol.

(3) Bis(4-nitrophenyl) carbonate: No more than 0.60 per cent was required to make all leathers of all sets of samples mildew resistant, and this concentration was required only for leathers B and C of the set of samples exposed to weathering at Yuma, Ariz., and for leather B of the set of samples exposed to weathering at NBS. In all other cases, no more then 0.30 per cent was required for prevention of mildew growth.

(4) N-(trichloromethylthio)tetrahydrophthalimide: This fungicide produced somewhat erratic results. The highest concentration used, 0.60 per cent, mildewproofed only one weathered sample, which was leather C of the samples exposed to weathering at NBS. Three unweathered samples were mildewproofed. These samples and the lowest concentrations required for

mildewproofness in each case were: Leather C, samples kept in NBS laboratory until tested for mildew resistance, 0.15 per cent; leather B, Panama samples, 0.60 per cent; and leather C, Panama samples, 0.15 per cent.

The fungicide apparently is sufficiently effective to mildewproof less mildew-susceptible leathers, such as leather C, under storage conditions at a concentration of about 0.60 per cent. Mildew growth on the more susceptible vegetable-tanned leathers can also be expected to be considerably inhibited by this concentration under storage conditions. The fungicide may be somewhat sensitive to weathering exposure. Although this characteristic was not clearly indicated in the field exposure study, it was very noticeable in the preliminary screening tests where the time interval between treatment of leather and test for mildew-resistance was much shorter [see section 3.9 (b)].

(5) Tetrachlorohydroquinone: The highest concentration used, 0.60 per cent, mildewproofed only leather A of the Yuma samples, leather A of the NBS unweathered samples, and leathers A and B of the Panama samples. The concentration levels required for mildew prevention in these four cases were 0.60, 0.60, 0.15, and 0.30 per cent, respectively.

This fungicide showed poor and erratic effectiveness in this field exposure test compared to the effectiveness shown in the tropical room screening tests in which 0.30 per cent had consistently provided mildewproofness of leather A (table 1). However, in earlier screening tests erratic behavior of this fungicide had been observed. It was thought then that it was due to an unsuitable formulation used, from which the fungicide had a tendency to precipitate. The formulation used in this investigation appeared to be stable for several months and, therefore, cannot be responsible for the erratic behavior.

Apparently tetrachlorohydroquinone is especially ineffective with leather C. Since this leather has a much higher oil content than leathers A and B, and tetrachlorohydroquinone is relatively insoluble in oil, it is suggested that these combined factors may be responsible for the observed behavior. It is possible that fluctuations in surrounding conditions bring about slow migration of the oil in a leather of high oil content. Through this process, after a considerable time the oil that comes to the surface of the leather may contain little, if any, of the oil-insoluble fungicide. The leather surfaces would then become mildew susceptible. If this is what happens, the oil solubility of a leather fungicide is a very important property from the standpoint of the fungicide's usefulness.

The possibility that tetrachlorohydroquinone is particularly ineffective with leather C because of the presence of chromium in this leather, contrasting to leathers A and B, seems unlikely but probably should not be excluded.

(6) 2-Phenylphenol and 4-chloro-m-xylenol: Only one case of mildewproofness was obtained with 2-phenylphenol. This was leather C of the Panama samples. None of the samples treated with 4-chloro-m-xylenol was mildew-

proofed. In view of the high concentration levels used, up to 1.70 per cent for 2-phenylphenol and up to 1.20 per cent for 4-chloro-m-xylenol, both fungicides are judged to be relatively ineffective mildewproofing agents for leather.

(d) *Correlation between field evaluation and screening tests*

Generally the results of this field exposure study show the same relative effectiveness of the fungicides as was previously found in screening tests where the tropical room exposure test was used (see section 3.1, table). However, tetrachlorohydroquinone proved less effective than was expected from the screening tests, mainly because it was so ineffective in the case of leather C, which was not used in screening tests. It has been assumed that a fungicide treatment that mildewproofs a vegetable-tanned leather will also mildewproof any other type of leather, since the former is more mildew susceptible. Apparently, there are exceptions to this generalization.

According to the initial screening test, as has already been indicated (section 3.1), leather containing 0.30 per cent of any of the fungicides included in this study was found to be mildew resistant, or very nearly so. The field performance cannot be correctly predicted from this test, except that all treatments failing to prevent mildew growth in the initial screening test can safely be assumed to fail under tropical jungle conditions. The tropical room exposure test may be assumed to predict fairly correctly the field performance under tropical jungle conditions and is the most dependable test available for evaluation of efficiencies of leather fungicides.

3.10 *Conclusions*

(a) In addition to 4-nitrophenol, it was found that 2-chloro-4-nitrophenol, 4-thiocyanophenol, and bis(4-nitrophenyl) carbonate prevent mildew growth on leathers under tropical jungle conditions at concentrations no higher than 0.60 per cent and are adequately stable under severe weathering conditions.

Compared to the effectiveness of 4-nitrophenol, 2-chloro-4-nitrophenol is slightly more effective, 4-thiocyanophenol is about equally effective, and bis (4-nitrophenyl) carbonate is slightly less effective, considering the over-all results of this study.

(b) N-(trichloromethylthio)tetrahydrophthalimide is moderately effective under storage conditions, but may be somewhat sensitive to severe weathering. At a concentration of 0.60 per cent this fungicide may be expected to mildewproof chrome retan leather and to considerably inhibit mildew growth on vegetable leathers under storage conditions.

(c) Tetrachlorohydroquinone gives erratic results and probably will not be dependable as a leather fungicide unless the causes of its erratic behavior are found and corrected.

(d) 2-Phenylphenol and 4-chloro-m-xylenol do not prevent or to any considerable extent inhibit mildew growth on leathers under severe mildew-growing conditions even at high concentrations (up to 1.70 per cent for 2-phenylphenol and up to 1.2 per cent for 4-chloro-m-xylenol).

(e) The tropical room exposure test for evaluation of leather fungicides predicts quite correctly the performance of the fungicides under the most severe mildew-growing conditions that may be encountered by military leather items. The agar plate test with *A. niger* and the ALCA mixed spores method (Methods 5011 and 5021 of Fed. Spec. KK-L-311a) are useful only as initial screening tests for leather fungicides. A fungicide treatment failing in these tests can safely be rejected. A fungicide treatment passing these tests will not necessarily be satisfactory under severe mildew-growing conditions in tropical jungles.

Acknowledgment

The authors acknowledge the cooperation by staff members of the Quartermaster Research and Development Field Evaluation Agency, Fort Lee, Virginia. The permission of the Office of the Chief of Engineers, U. S. Army, to use the tropical room at the Engineering Center, Fort Belvoir, Va., is greatly appreciated.

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Appendix—Climatological Conditions

1. *Yuma, Arizona (observations at Yuma Test Station, Yuma, Ariz.)*

Period	No. of daily observations made	Temperature			Relative humidity			Precipitation		
		Mean	Maximum	Minimum	Mean	Maximum	Minimum	Total	Frequency	Daily average
		°F	°F	°F	Per cent	Per cent	Per cent	in.	days	in.
1954										
July 6–31	26	93.5	116.0	75	47.2	96	15	0.19	3	0.007
Aug. 1–31	30	90.4	115.0	56	41.2	82	10	0.11	1	0.004
Sept. 1–30	30	89.4	108.0	69	35.9	90	5	0.24	2	0.008
Oct. 1–6	6	81.5	100.0	64	40.8	80	10	0.00	0	0.000
Average for total period		88.7	109.8	66	41.3	87	10			0.006

2. *Washington, D. C. (observations at National Airport)*

July 6–31	26	78.7	103.0	62	62	94	24.0	1.09	7	0.16
Aug. 1–31	31	75.4	94.0	58	68	96	34.0	3.15	11	0.29
Sept. 1–30	30	73.5	99.0	50	67	95	32.0	0.63	8	0.08
Oct. 1–6	6	76.5	94.0	54	75	95	40.0	0.45	3	0.15
Average for Total period		76.0	97.5	56	68	95	32.5			0.17

3. *Panama Test Sites* (temperature and relative humidity observations were obtained with a hygrothermograph located in the shelter with the leather samples. The observations on precipitation were obtained from the Naval Research Laboratory Tropical Experimental Station, Coco Solo Naval Station, Panama Canal Zone.)

Site	Period	No of daily observations made	Temperature			Relative humidity			Precipitation		
			Mean	Maximum	Minimum	Mean	Maximum	Minimum	Total	Frequency	Daily average
			°F	°F	°F	Per cent	Per cent	Per cent	in.	days	in.
1*	June 30–July 15	15	81.0	108	59	62.5	97	30	7.34	9	0.49
2**	July 16–Aug. 3	19	80.0	90	71	83.4	100	58	5.70	14	0.30
3***	Aug. 4–Oct. 28	86	78.7	90	72	86.5	99	51	35.75	67	0.53

* Cotozal General Depot, U. S. Army, cleared area.
** Cotozal General Depot, U. S. Army, thin jungle area.
*** Jungle Hut of the Naval Research Laboratory Tropical Exposure Station, Galata Road, near Coco Solo Naval Station.

No mildew grew on any of the samples during exposure at sites 1 and 2. The data on mildew growth were obtained during the exposure at site 3.

4. *Tropical room at the Engineering Center, U. S. Army, Fort Belvoir, Virginia.*

Daily cycle of temperature and relative humidity.

0400—0800 hours 75°F, 95 per cent relative humidity.
0800—1200 hours Temperature increasing from 75° F to 85° F and relative humidity decreasing from 95 per cent to 90 per cent.
1200—2000 hours 85° F, 90 per cent relative humidity.
2000—0400 hours Temperature decreasing from 85° F to 75° F and relative humidity increasing from 90 per cent to 95 per cent.

BOOK REVIEW

Gerbereichemisches Taschenbuch (Leather Chemistry Pocket Book), A. Küntzel. Sixth completely revised edition. Theodore Steinkopf, Dresden and Leipzig, 1955. XI+319 pp. Price, $4.20.

The first edition of this work (1927) was initiated by Dr. Edmund Stiasny and was edited by Dr. C. Riess. As the number of editions has mounted, the scope of the work has been expanded, the format enlarged, and the number of pages at least doubled. This, the sixth edition, barely qualifies as a "pocket book" in the literal sense.

The book remains a laboratory manual covering the analysis and testing of leather and the materials used in producing it. However, it is much more than a handy compilation of

routine methods. Many of the methods have to do with the identification, characterization, and laboratory appraisal of new materials—new to the leather industry or more likely new to a particular tannery. These portions of the book will be most useful to American leather chemists. Few of us will consult the pages describing the determination of tannin, or the determination of chromium in liquor or leathers. Many of us, if fortunate enough to be able to read Prof. Küntzel's lucid German, will thank the author for the sections on technical evaluation of tannins, synthetic tannins, investigation of dyes, and investigation of finishes, to name only a few examples. Perusal of these parts of the book, will, at the least, save the analyst many a time-consuming search through journal files, and may reveal the existence of methods that he has forgotten about, or never knew existed.

The book consists of twenty chapters, as follows: I. Volumetric Analysis, II. Determination of pH value (by indicators or by the glass electrode), III. Protein Chemistry Investigations, IV. Preparation and Staining of Microsections of Skin, V. Water (including general requirements, analysis, softening, sewage, and bacteriological examination), VI. Alkalies, Sulphides, and Unhairing Liquors, VII. Acids and Salts, VIII. Enzyme Bates, IX. Chromium Salts (including reducing agents, determination of neutral salts, basicity, and masking agents in chrome liquors, and chromium and basicity in leather), X. Other Minerals Tanning Agents (aluminum, zirconium, and polymeric phosphates) XI. Vegetable Tannins (much the longest chapter, 80 pages), XII. Synthetic Tannins, XIII. Lignin Extracts, XIV. Formaldehyde, XV. Fats and Oils for Leather, XVI. Investigation of Leather Dyes (edited by G. Otto), XVII. Investigation of Finishes (edited by K. Eitel), XVIII. Investigation of Leather Laquers, XIX. Investigation of Leather (sampling, chemical analysis, physical tests, wear tests, aging tests and microscopic examination), XX. Tables.

The description of the methods are brief but adequate. It is apparent that the book is addressed to trained analysts, not to students. Similarly the sections on bacteriology (chapter V), and microscopy (chapters IV and XIX) will not be of much use to one untrained in bacteriological and histological techniques. No formal bibliographies are provided, but numerous references to original papers are run in with the text. American and British journals appear to have been very well covered. The price is reasonable.

H. B. Merrill

ABSTRACTS

Practical Experiences with Paste Drying of Leather. By F. Kahne. *The Tanner*, **10,** No. 4, 12, No. 5, 15 and No. 6, 23 (1955). The author draws his conclusions from 18 months experimentation on many kinds of leathers in an American plant. It was soon learned that no one paste can possibly be suitable for all leathers. The ingredients tried included wheat, rice and corn starches, carob bean husk flour, manioka, glucose, island dough, gum tragacanth and water soluble cellulose products. A paste must be easily prepared and the addition of a preservative is indispensable, as spoiling is very rapid. Two pastes found useful are: Paste I, 2kg. methyl cellulose, 0.5kg. casein and 170kg. water. Paste II, 1000 parts carob bean husk flour, 2000 parts glucose and 600 parts sulfonated neats foot oil. Glass, enamelled metal and plastic surface plates are all used. Glass is recommended. It is pointed out that, particularly with box calf, paste drying produces quite a different leather than that dried in the usual way. Consequently the entire tanning operation must be adjusted to this change. Methods such as increasing fat liquor, adding lubricants or fillers during or after tanning and dyeing in order to give paste dried box calf properties similar to normally dried leather are possible but dangerous. Adjustments with

vegetable and synthetic tanning materials, use of highly concentrated and high basic chrome liquors and slow drying at low temperatures are suggested. In applying the leather to the drying plates, metal slickers are not recommended. Since paste dried leathers are particularly sensitive to cracks and breaks, they should be handled with great care. The paste must be completely washed from the leather before finishing. Sawdusting before staking is advantageous. In general, paste drying gives leather of exceptional form and smoothness. Semichrome and vegetable tanned leathers are particularly suited to paste drying. In the case of suede leather and chrome splits, in spite of many trials, no useful results were attained.

Hopea Parviflora Bark as a Suitable Substitute for Imported Wattle Bark. By P. S. Chowdary, K. A. Joseph and K. Padmanabhan. *The Tanner*, **10,** No. 6, 17, (1955). Hopea Parviflora (Iron Wood of Malabar) was satisfactorily used for making kip leather with the following modification. After traditional liming and deliming, the hides were pickled with 2 per cent formic acid and 10 per cent salt. After depickling, using hypo and salt, the hides were given a pre-tanning with 1 per cent Basyntan on pelt weight. Following this the hides were tanned and finished as usual. The leather was superior to wattle tanned kips in color, feel and fullness. A blend of 65 per cent hopea parviflora bark with 35 per cent myrobalams gave a sole leather of superior qualities. It is concluded that this tannin material can be used as a substitute for wattle. The bark is obtained as a by-product of the lumber industry.

Liquid Neoprene Coatings. *Corrosion Technology*, **2,** No. 7, 213 (1955). The required properties of an ideal corrosion preventive coating are: 1. It should adhere tenaciously. 2. It should be readily applied, giving a pinhole free film having a minimum thickness of 2 mil. per coat. 3. It should cure rapidly to a film completely resistant to solvents, acids, alkalis and salts at temperature up to 200 degrees F. 4. It should be unaffected by sunlight and weather. 5. It should have high tensile strength and elongation. 6. It's properties should be permanent for all practical purposes. 7. It should be available in a wide variety of colors. 8. It should not require special curing technique and should be reasonably non toxic to the applicator. 9. It should have a long record of successful use. 10. It should be economical and available commercially. 11. It should withstand abrasion and shock. Liquid Neoprene surface coatings approach these ideal conditions more nearly than any other commercially available coating material. The article describes method of application and various large scale uses.

The Solvent Scouring of Grease Wool. I—Review. By D. P. Norman and W. W. A. Johnson. *American Dyestuffs Reporter*, **44,** No. 26, 893 (1955). The authors review principles and practices of the solvent scouring of wool in the light of current knowledge of solvent extraction as an engineering process. Operations and terminology common to all solvent extraction systems are defined and illustrated. The problems, peculiar to wool scouring, are described in detail. Much information about wool grease needed for design of a rational solvent scouring system, particularly with regard to solvents, is still not available. Five flow sheets and figures illustrating solvent extraction systems and equipment are given. Three tables show constitution of wool and wool grease together with impurities present.

The Three Positions of Sampling Sole Leather. By C. G. Telander and J. F. Wagoner. *Shoe and Leather Reporter*, **280,** No. 12, 13 (1955). A whole pack of sole leather was cut into 6 strips and each strip into soles as illustrated in Fig. I. All were analysed individually, as a whole and layerwise. The results confirm the well known fact that tannage is

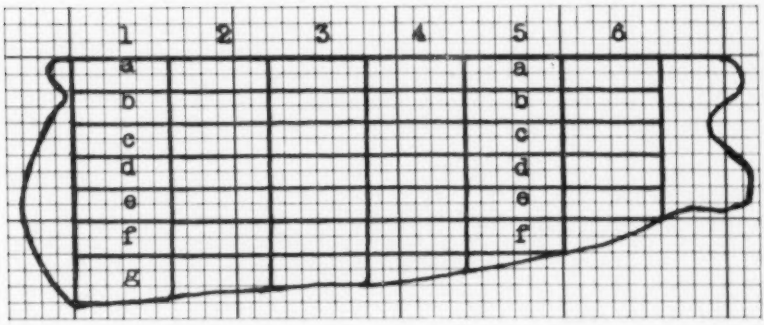


FIGURE I. Showing Strip and Sole Location

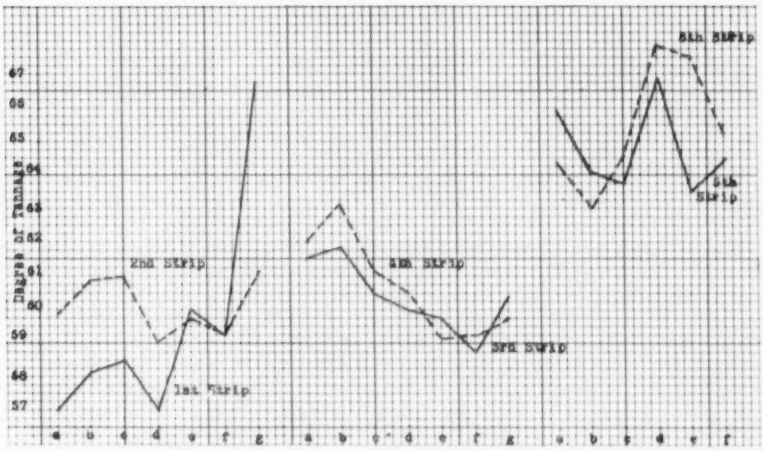


FIGURE II. Degree Tannage Distribution in Strip & Sole Location

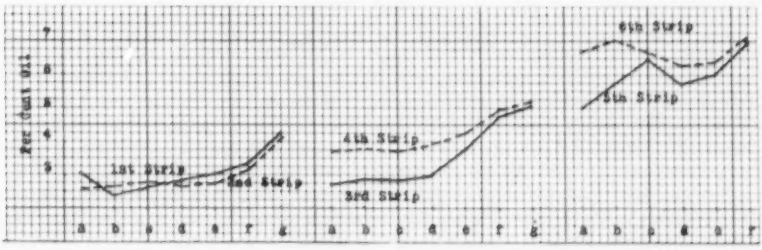


FIGURE III. Oil Distribution in Strip and Sole Location

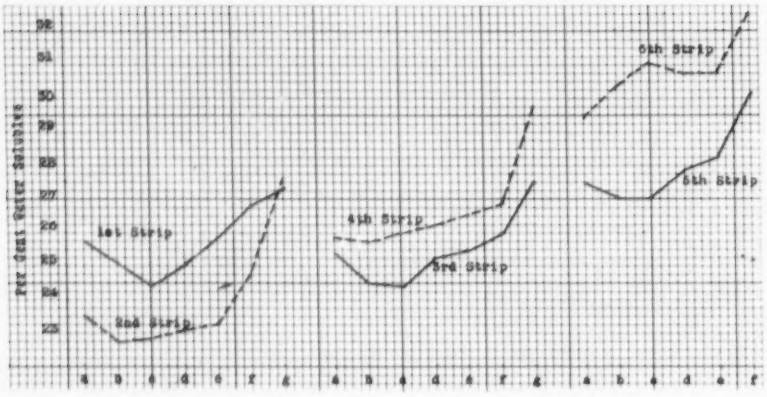
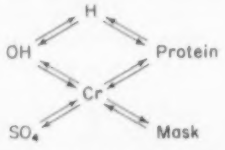


FIGURE IV. Water Solubles Distribution in Strip and Sole Location

not uniform either area-wise or cross section wise. However the sum total of the data confirmed that the three position sampling as recommended by the A.L.C.A. committee on sampling in 1921 gives almost the same result as obtained by analysis of all the soles. Therefore the three position sampling method should be retained. Fig. II illustrates the degree of tannage distribution, Fig. III the oil distribution, and Fig. IV the water solubles distribution in strip and sole locations.

Modern Trends in Chrome Tanning. By T. C. Thorstensen. *The Leather Manufacturer.* **72,** No. 21, 8 (1955). This is primarily a correlation of accepted facts of chemistry and practical chrome tanning. The chromium atom is exposed to the effect of hydrogen and hydroxyl ions, as regulated by basicity, by sulfate ions if chromium sulfate is used, and by masking agents. Since the hydrogen ions do not directly combine with the chromium, there are four simultaneous reactions between chromium and those reactors tending to come to equilibrium, although complete equilibrium is probably never reached in practical tanning. The situation is graphically represented as shown.



In controlling the equilibriums established, pH is of prime importance. The higher the pH the more readily the chromium combines with the protein. Hence it is practice to start with a low pH (usually around 2.0 or 2.5) to allow penetration to the center of the hide without much fixation. Then pH is raised by treatment with sodium bicarbonate, or other mild alkali, and true tannage takes place. Since de-liming and pickling have much effect on the condition of the hide, with regard to these reactions, their importance is obvious. Masking agents tend to protect the chromium atom from the other reactions. The object is to partially protect it, until penetration is complete, and then allow the reaction with the protein to take place with the rise in pH. For this purpose, formate has so far proved best.

Acetate holds the chrome more firmly, citrate more so and oxalate holds it very firmly. Even with formate a somewhat higher pH must be attained to accomplish satisfactory combination with the protein. Temperature is also of vital importance and must be carefully controlled since, as in most chemical reactions, the equilibriums shift with temperature change. With regard to the future, there are possibilities of introducing oils or high polyiners with beneficial effects. Researches have indicated that simultaneous chrome and vegetable tanning is possible.

The Use of Petroleum Products in Leather. By W. J. Fleming. The *Leather Manufacturer*, **72,** No. 12, 31 (1955). Petroleum oils acquired a bad name in the tanning industry in the early days because not fully refined. Such impurities as asphaltic bodies and sulfur precipitated on the leather or developed acidity which atacked the fibers. However the fully purified petroleum products are now in general use. Straight petroleum oils are limited principally to the finish oiling operations. Sole leather oiling mixtures may run as high as 90 per cent petroleum oil. Petroleum leather oils do not differ chemically from lubricating oils, but are carefully selected for specific services. All mineral oils are completely hydrophobic, differing from fatty oils which have some hydrophilic groups. Consequently mineral oils show high interfacial tension. As little as 1 per cent oleic acid can reduce the interfacial tension into the region of the fatty oils. Important properties of mineral oils are: (1) greater uniformity than normally found in natural fats, (2) high resistance to oxidation and attack by micro-organisms, (3) rapid penetration of leather, (4) improves water repellency, (5) does not spue. Waxes are classified as ordinary paraffin and microcrystalline waxes. Use of paraffin waxes is largely confined to filling and firming agents in currying mixtures and, mixed with microcrystalline waxes, to supply firmness and penetrating properties. Microcrystalline waxes, because of their minute crystalline structure which imparts flexibility, ductility and plasticity are used in the water-proofing treatment of chrome retan sole leather. Petrolatums (petroleum jellies) are used in currying and water proofing mixtures as platicizers. Sulfonated mineral oils differ from sulfated fatty oils in that the sulfur is combined directly with the carbon atom in the former and through an oxygen, in an ester linkage, in the latter. It has been established that it is the free oil in a sulfated fatty oil which lubricates. The actual sulfo oil fraction combines with the leather and does not contribute to either softness or fullness. Mineral oil sulfonates function similarly but combine with the leather with greater affinity. They are not hydrolyzed on aging. They do not form sulfuric acid on aging and possess some of the the characteristics of tanning agents. They have little or no lubricating capacity. This may be attained by adding free fatty oil. Petroleum solvents, usually Stoddard Solvent, are mostly used for degreasing pigskin and pickled sheepskins.

Behavior of Dowex-50 as an Aminopeptidase. J. R. Whitaker and F. E. Deatherage. *J.A.C.S.*, **77,** No. 20, 5298 (1955). It has been previously reported that Dowex-50 is an excellent catalyst for hydrolyzing some proteins. Does it act as an insoluble "strong acid", a surface active solid, or a highly hydrated polymer showing certain membrane phenomena? Why is it selective in it's action on proteins and peptides? The present work is concerned with requirements for, and the mechanism of, hydrolysis of the peptide linkage by Dowex-50 and indicates that this sulfonated polystyrene resin shows some properties similar to certain enzymes. Dowex-50 requires a free amino group for its catalytic activity. At 104° Dowex-50 splits glycylglycine very rapidly compared to acetylglycine. Aspargine is also split more rapidly by Dowex-50 than is acetamide. Because of the complex formed between the amino group of the substrate and the charged sulfonate group of the resin, the peptide bond is placed under a strain which permits easier splitting of the bond. The formation of the resin-substrate complex can be mathematically treated in the same manner

as is used for the treatment of enzyme systems. The nature of the substrate, temperature, pH of the medium and inhibitors affect the dissociation constant of the resin-substrate complex.

PATENTS

Soaking Hides. Brit. Pat. 730,697. Dow Chemical Co. Apl. June 3, 1953. Freshly flayed hides (including furs) are washed and soaked prior to liming and tanning, in the presence of one or more of the compounds diethanol glycine, ethylenediaminetetraacetic acid, propylenediaminetetraacetic acid, triethylenediaminetetraacetic acid, 1,2-diaminocyclohexanetetraacetic acid, monohydroxyethyl-ethylenediaminetriacetic acid and monobenzylethylenediaminetriacetic acid, or an alkali metal or amine salt thereof, in aqueous medium. A sufficient quantity of the amino acid or salt to soften the water completely and additionally equal to 0.1—0.3 per cent by weight of the hides is preferably used. In the example, 12 pounds of a mixture of equal parts of the sodium salts of diethanol glycine and ethylenediaminetetraacetic acid were added to 4,250 lbs. of brine-cured cowhides in 12,750 lbs of water at 65°F. The initial pH of 9 fell to 8 after 18 hours. The hides were subsequently treated in conventional manner for vegetable tanning and chrome retaining.

Softening Hides and Skins. Brit. Pat. 730,895. Boehme Fettchemie Ges. Apl. Oct. 27, 1952. In a process for softening animal hides or skins the softening liquor contains at least one antibiotic or a material containing it, to prevent growth of injurious bacteria. The preferred antibiotics have a polypeptide structure and actinomycin, aureomycin and penicillin are specified. These may be employed pure or as culture solutions or crude concentrates. The concentration of antibiotic employed may be from 0.000001 to 0.01 per cent. The antibiotic may have surface active properties but surface active agents, softening agents, disinfectants and preservatives may be added to the softening liquor. According to an example, sun dried hides are softened at 15—20°C. in a softening liquor containing 0.001 per cent actinomycin and 0.005 per cent by weight of aureomycin. A ricinoleic acid butyl ester sulphonate may be added as a softening agent.

Improving Damaged Hides. Brit. Pat. 732,010. Laimbock, J. B. Apl. June 11, 1953. Skins, hides and leather damaged, e.g. by barbed wire, or when skinning, or by salt-stains, are abraded before or after dyeing through openings in a stencil, said openings being chosen to form a pattern and expose the damaged places in the skin. Abrasion may be by means of a jet of hard fine particles such as of sand, steel, glass or carborundum, or by means of cards or brushes or emery paper, steel wool, shark or watersnake skins. If desired, counter-pressure may be applied to the skin opposite the openings in the stencil. The treatment may be applied to either side of the skin. In the case of an undyed skin, dyeing produces a design in which the abraded portions are darker: with dyed skins, the abraded portion is lighter. Colors may subsequently be applied through the same stencil by brushing or spraying. Abrasion may if desired be continued until a perforated pattern is obtained.

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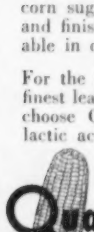

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